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Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA, IRVINE

Methods of Calculation with the Exact Density Functional using the Renormalization Group

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Physics

by

Thomas Edward Baker

Dissertation Committee: Professor Kieron Burke, Chair Professor Steven R. White Professor Filip Furche Professor Clare Yu

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DEDICATION

Honest to god, I didn't think it'd be hard to pick all of the bones in the graveyard. The entropy will never be lower.

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PUBLICATIONS

- [15] **T.E. Baker**, K. Burke, and S.R. White <u>Chemical accuracy from small, system-adapted basis functions</u> *submitted*
- [14] A. Tkatchenko, M. Afzal, C, Anderson, T. Baker, R. Banisch, S. Chiama, C. Draxl, M. Haghighatlari, F. Heidar-Zadeh, M. Hirn, J. Hoja, O. Isayev, R. Kondor, L. Li, Y. Li, G. Martyna, M. Meila, K.S. Ruiz, M. Rupp, H. Sauceda, A. Shapeev, M. Stöhr, K.-R. Müller, S. Shankar, Recent Progress and Open Problems *IPAM Program on Machine Learning & Many-Particle Systems* (2017) avail. online
- [13] C. Garcia-Cervera and **T.E. Baker**, <u>IPAM Book of DFT: The Quantum *N*-body Problem* *submitted*</u>
- [12] J.P. Perdew and **T.E. Baker**, <u>IPAM Book of DFT: Generalized Gradient Approximations</u>^{*} submitted (*-as part of Putting the Theory Back in Density Functional Theory)
- [11] L. Li (), T.E. Baker, S.R. White, K. Burke, <u>Pure density functional for strong</u> correlations and the thermodynamic limit from machine learning *Phys. Rev. B* 94, 245129 (2016) [arXiv:1609.03705]
- [10] **T.E. Baker**, A. Richie-Halford, and A. Bill, <u>Classification of pair corre-</u> lations and $0 - \pi$ transitions in superconducting-magnetic hybrid structures *Phys. Rev. B* **94**, 104518 (2016) [arXiv:1606.05567]
- [9] **T.E. Baker**, <u>Reproducing sterile neutrinos and the behavior of flavor oscilla-</u> tions with superconducting-magnetic proximity effects [arXiv:1601.00913]
- [8] T.E. Baker and A. Bill, Effects from magnetic boundary conditions in superconducting-magnetic proximity systems AIP Advances 6, 055811 (2016)^{*} (*-As part of the 2016 Joint MMM Conference)
- T.E. Baker, E.M. Stoudenmire, L.O. Wagner, K. Burke, and S.R. White, One dimensional mimicking of electronic structure: the case for exponentials *Phys. Rev. B* 91, 235141 (2015) [arXiv:1504.05620]
- [6] L.O. Wagner, T.E. Baker, E.M. Stoudenmire, K. Burke, and S.R. White, Kohn-Sham calculations with the exact functional *Phys. Rev. B* 90, 045109 (2014) [Editor's Choice] [arXiv:1405.0864]
- [5] **T.E. Baker**, A. Richie-Halford, O.E. Icreverzi, and A. Bill, <u>Cascading prox-</u> imity effects in rotating magnetizations *Europhys. Lett.* **107**, 17001 (2014) [arXiv:1403.4149]
- [4] **T.E. Baker**, A. Richie-Halford, and A. Bill, Long range triplet Josephson current and the 0π transition in tunable domain walls *New J. Phys.* **16**, 093048 (2014) [Video Abstract] [arXiv:1310.6580]

- [3] A. Bill, J. de Rojas, **T.E. Baker**, and A. Richie-Halford, Properties of magnetic-superconducting proximity systems *J. Super. Novel* $\overline{Mag. 25, 27}$ $\overline{(2012)^{\dagger}}$
- [2] **T.E. Baker**, O.E. Icreverzi, and A. Bill, Classical mechanical analogies in wide dirty SFS junctions *J. Super. Novel Mag.* **25**, 7 (2012)[†] ([†]-As part of the *Trends on Superconductivity and Novel Magnetism*)
- [1] **T.E. Baker** and A. Bill, Jacobi elliptic functions and the complete solution to the bead on the hoop problem *Am. J. Phys.* **80**, 506 (2012) [Featured] [arXiv:1201.4201]

CONFERENCE PRESENTATIONS & COLLOQUIA

Canadian-American-Mexican Graduate Student Physics ConferenceAugust 20172017 Washington D.C., USACategorization of effects and novel physics in superconducting-magneticproximity systems[Presentation: T.E. Baker]Session Chair: Atomic, Molecular, and Optical Physics

2017 Associated Graduate Students Graduate Research SymposiumApril 2017Irvine, CA, USAUnderstanding neutrino oscillations with superconductors and magneticfields[Presentation: T.E. Baker][Presentation: T.E. Baker]

American Physical Society March Meeting New Orleans, LA, USA	March 2017	
Investigating density functional theory with the density matrix renormaliza-		
tion group		
[Presentation: T.E. Baker]		

Group meeting of J.D. Whitfield Dartmouth, Connecticut, USAMarch 2017Probing the structure of density functional theory with the density matrix
renormalization groupRemote Presentation: T.E. Baker]

Université de Sherbrooke Département de Physique Colloque Québec, February 2017 Canada Categorization of effects and novel physics in superconducting-magnetic proximity systems [Presentation: T.E. Baker]

Culminating Retreat - Understanding Many-Particle Systems with Machine Learning Lake Arrowhead, CA, USA Using Wavelets to Make an Adapted Basis Set

[Presentation: T.E. Baker, A. Kesselman, G. Evenbly, Steven R. White, and Kieron Burke]	
American Physical Society Far West Section Meeting Davis, CA, USA Using Wavelets to Make an Adapted Basis Set [Presentation: T.E. Baker, G. Evenbly, A. Kesselman, K. Burke, S.R. White]	October 2016
American Physical Society April Meeting Salt Lake City, UT, USA <i>Reproducing sterile neutrinos and the behavior of flavor oscillations with</i> <i>superconducting-magnetic proximity effects</i> [Presentation: T.E. Baker]	April 2016
American Physical Society March Meeting Baltimore, MD, USA Tests for Wavelets as a Basis Set [Presentation: T.F. Baker, G. Evenbly, A. Kesselman, K. Burke, S.R. White]	March 2016
CSU Fresno Physics Department Colloquium (Hosted by D. Singleton) Fresno, CA, USA <i>Reproducing sterile neutrinos and the behavior of flavor oscillations with</i> <i>superconducting-magnetic proximity effects</i> [Presentation: T.E. Baker]	February 2016
UC Irvine Astrophysics Theory Journal Club (Hosted by A. Grauss) Irvine, CA, USA Reproducing sterile neutrinos and the behavior of flavor oscillations with superconducting-magnetic proximity effects [Presentation: T.E. Baker]	February 2016
UC Irvine Particle Theory Journal Club (Hosted by F. Tanedo and T. Tait) Irvine, CA, USA Reproducing sterile neutrinos and the behavior of flavor oscillations with superconducting-magnetic proximity effects [Presentation: T.E. Baker]	February 2016
2016 Joint MMM-Intermag Conference San Diego, CA, USA <i>Comparative Study of Pair Correlations in Superconducting-Magnetic Hybrid</i> <i>Systems</i> [Presentation: T.E. Baker, A. Richie-Halford, A. Bill]	January 2016
American Physical Society Far West Section Meeting Long Beach, CA, USA Probing the Structure of Density Functional Theory with Density Matrix Renormalization Group [Presentation: T.E. Baker, L. Li, K. Burke, S.R. White]	October 2015

American Physical Society March Meeting San Antonio, TX, USA Band Gap Studies in Density Functional Theory [Presentation: T.E. Baker, E.M. Stoudenmire, L.O. Wagner, K. Burke, S.R. White]	March 2015
Advanced Numerical Algorithms for Strongly Correlated Quantum Sys- tems [§] Würzburg, Germany Probing the Failures of DFT with Computationally Efficient Interactions and	February 2015
DMRG [Selected for Contributed Talk: T.E. Baker, L.O. Wagner, E.M. Stouden- mire, K. Burke, S.R. White] [§] -hosted by FOR 1807	
Group Meeting of E.K.U. Gross Halle, Germany Persistent Singlet Cascades and $0 - \pi$ Transition Typology in Superconductor- Exchange Spring and Other Magnetic Hybrid Systems [Talk: T.E. Baker, A. Richie-Halford, A. Bill]	February 2015
American Physical Society Far West Section 2014 Annual Meeting Reno, NV USA	October 2014
Cascading Proximity Effects in Inhomogeneous Superconductor- Ferromagnetic Structures [Presentation: T.E. Baker, A. Richie-Halford, A. Bill]	
American Physical Society March Meeting Denver, CO, USA Benchmarking Density Functional Theory with Density Matrix Renormaliza- tion Group and Lessons For Higher Dimensions [Presentation: T.E. Baker, L.O. Wagner, E.M. Stoudenmire, S.R. White, and K. Burke]	March 2014
 American Physical Society Far West Section Meeting Sonoma, CA, USA Long Range Effects in Tunable Superconducting-Magnetic Proximity Systems [Presentation: T.E. Baker, A. Richie-Halford, O.E. Icreverzi, A. Bill] Winner 1st place: Kennedy Reed Award for Best Theoretical Research by a Graduate Student 	November 2013
American Physical Society March Meeting Baltimore, MD, USA Analytic Description of Superconducting-Ferromagnetic Proximity Systems [Presentation: T.E. Baker, O.E. Icreverzi, A. Moke, A. Bill]	March 2013
California State University Student Research Competition (State) Long Beach, CA, USA <i>The Bead on a Hoop and Ferromagnetism: An Analogy Between Classical</i> <i>Mechanics and Magnetism</i>	May 2012
[Presentation: T.E. Baker, A. Richie-Halford, A. Bill] Winner 1 st place: Mathematical and Physical Sciences category	

California State University Student Research Competition (Local) Long Beach CA USA	February 2012
The Bead on a Hoop and Ferromagnetism: An Analogy Between Classical	
Mechanics and Magnetism	
[Presentation: T.E. Baker, A. Richie-Halford, O.E. Icreverzi, A. Bill]	
winner 1 ^{ee} place: Mathematical and Physical Sciences category	
American Physical Society California-Nevada Section 2011 Annual Meet-	October 2011
Jacobi Elliptic Functions and their Application to Classical Mechanics, Su-	
perconductivity, and Magnetism	
[Presentation: T.E. Baker, A. Richie-Halford, A. Bill]	
Winner 1 st place: Kennedy Reed Award for Best Theoretical Research by a	
Graduate Student	
OSTER PRESENTATIONS	
Southern California Theoretical Chemistry Symposium 2.0 Irvine, CA, USA	May 2017
Approximating Natural Orbitals with a Product Plane Wave Ansatz	
[Poster: T.E. Baker, Kieron Burke, and Steven R. White]	
UCI Chemistry Department Prospective Student Tour Irvine, CA, USA	March 2017
Density Functional Methods in Quantum Mechanics	
[Poster: Burke Group (made by T.E. Baker)]	
Many Electron Collaboration Annual Meeting New York, NY, USA	February 2017
Approximating Natural Orbitals with a Product Plane Wave Ansatz	J. J
[Poster: T.E. Baker, Kieron Burke, and Steven R. White]	
Symposium on Recent Advances in Data Science Irvine, CA, USA	October 2016
Pure density functional theory with machine learning	
[Poster: T.E. Baker, Li Li, S.R. White, K. Burke]	
1 st Southern California Theoretical Chemistry Symposium La Jolla, CA,	June 2016
USA	
[Poster: T.E. Baker, G. Evenbly, A. Kesselman, K. Burke, S.R. White]	
Many Electron Collaboration Annual Meeting New York, NY, USA	February 2016
Speeding up strongly correlated calculations: Wavelet coarse graining	
[rusici. 1.1. dakei, O. Evenuiy, A. Kessennan, K. duike, S.K. while]	

 Ψ-k-2015 Conference San Sebastian-Donostia San Sebastian, Spain Low Cost Mimicry of the Soft-Coulomb with Exponential Interactions [Poster: T.E. Baker, E.M. Stoudenmire, L.O. Wagner, K. Burke, S.R. White] 	September 2015
Many Electron Collaboration Annual Meeting New York, NY, USA Low Cost Mimicry of the Soft-Coulomb with Exponential Interactions [Poster: T.E. Baker, E.M. Stoudenmire, L.O. Wagner, K. Burke, S.R. White]	February 2015
Materials and Mechanisms of Superconductivity Washington D.C., USA Long Range Triplet Superconducting Effects in a Ferromagnetic Josephson Junction [Poster: T.E. Baker, A. Richie-Halford, A. Moke, A. Bill]	July 2012
University Achievement Awards and Celebration of Instruction, Re-	April 2012
search Long Beach, CA, USA <i>Triplet Superconducting Proximity Effects in Variable Magnetic Profiles</i> [Poster: T.E. Baker, A. Richie-Halford, O.E. Icreverzi, A. Moke, M. Campos, A. Bill]	
California State University, Long Beach College of Natural Sciences and Mathematics Student Research Symposium Long Beach, CA, USA <i>Exact Determination of Green's Functions in a Bulk Superconductor</i> [Poster: O.E. Icreverzi, T.E. Baker, A. Bill]	September 2011
Trends on Superconductivity and Novel Magnetism Cali, Colombia <i>Classical Mechanical Analogies in Magnetic Thin Films</i> [Poster: T.E. Baker, A. Bill]	June 2011
University Achievement Awards and Celebration of Instruction, Re- search Long Beach, CA, USA <i>The Bead and the Hoop as a Model for Magnetic Thin Films</i> [Poster: T.E. Baker, A. Bill]	April 2011
California State University, Long Beach College of Natural Sciences and Mathematics Faculty Research Symposium Long Beach, CA, USA <i>The Bead and the Hoop as a Model for Magnetic Thin Films</i> [Poster: T.E. Baker, A. Bill]	March 2011
SCHOOLS & WORKSHOPS	
Simons Collaboration on the Many Electron Problem: Quantum Monte Carlo Methods Stonybrook, NY, USA	June 2017

Data Science Initiative: A Deep Intro to Julia Irvine, California USAOctober 2016

Tutorials in: julia

7th Time-Dependent Density-Functional Theory: Prospects and Applica- September 2016 tions Benasque, Spain Tutorials in: Octopus, BerkeleyGW Pure density functional theory with machine learning [Poster: T.E. Baker, L. Li, S.R. White, K. Burke] Putting the Theory Back in Density Functional Theory Institute for Pure **August 2016** and Applied Mathematics, Los Angeles, CA, USA Pure density functional theory with machine learning [Poster: T.E. Baker, L. Li, S.R. White, K. Burke] Simons Collaboration on the Many Electron Problem: Entanglement **June 2016 Renormalization Methods & Diagrammatic Quantum Monte Carlo** Stonybrook, NY, USA Optimized basis sets from wavelet transformations [Presentation: T.E. Baker, G. Evenbly, A. Kesselman, K. Burke, S.R. White] Many Electron Collaboration Mini-Meeting (Hosted by S.R. White) **August 2015** Irvine, CA, USA Probing the Failures of DFT with DMRG [Presentation: T.E. Baker] **Doctoral Training in Statistical Mechanics** Les Houches, France June 2015 Simons Collaboration on the Many Electron Problem: Dynamical Mean June 2015 Field Theory & Tensor Networks Stonybrook, NY, USA Benchmarking Density Functional Theory with Density Matrix Renormalization Group and Lessons For Higher Dimensions [Presentation: T.E. Baker, E.M. Stoudenmire, L.O. Wagner, K. Burke, S.R. White] Hands-on Summer School: Electronic Structure Theory for Materials **July 2014** and (Bio)molecules Institute for Pure and Applied Mathematics, Los Angeles, CA, USA Tutorials in: FHI-aims Consequences of the Guaranteed Convergence of the Kohn-Sham Equations with Comparisons to Density Matrix Renormalization Group [Poster: T.E. Baker, L.O. Wagner, E.M. Stoudenmire, K. Burke, and S.R. White] 2014 International Summer School on Computational Methods for May 2014 Quantum Materials Hosted by U. Sherbrooke, Canada

Tutorials in: Abinit, Wein2k, ITensor

Consequences of the Guaranteed Convergence of the Kohn-Sham Equations with Comparisons to Density Matrix Renormalization Group

[Poster: T.E. Baker, L.O. Wagner, E.M. Stoudenmire, K. Burke, and S.R. White]

HONORS

• Forum on Graduate Student Affairs travel award for Canadian-American- Mexican Graduate Student Physics Conference (\$250)	August 2017
Associated Graduate Students (UC Irvine) Travel Award (\$400)	February 2017
American Physical Society's Division of Condensed Matter Physics Grad-	January 2017
uate Student Travel Award (\$500)	0
• Travel Award: University of California, Irvine (\$250 for 2017 March APS	December 2016
Meeting)	
• UCI Sigma Xi Chapter Best Poster (\$79.95)	March 2016
• UCI Sigma Xi Chapter Best Poster (\$65)	March 2015
• Associated Graduate Students (UC Irvine) Travel Award (\$600)	February 2015
• American Physical Society's Forum on Graduate Students Association	February 2015
Travel Award (\$500)	
• Orange County Chapter of the Achievement Rewards for College Scientists	2014-2016
(ARCS) Foundation Fellowship (Pat Beckman Memorial Scholar, \$15,000	
total over 2 years)	
• University of California, Irvine Travel Award (\$250 for 2014 March APS	March 2014
Meeting)	
• Kennedy Reed Award for Best Theoretical Research by a Graduate Stu-	October 2013
dent (1 st place, \$250) [American Physical Society California-Nevada Section	
2013 Annual Meeting]	Manak 2012
• Iravel Award: University of California, Irvine (\$250 for 2013 March APS	March 2013
Meeting)	2012 2014
• University of Camornia Regents Fellowship (\$10,000 total over 2 years) • Mathematical and Dhysical Sciences division at the California State Univer	2012-2014 May 2012
• Wathematical and Flysical Sciences division at the California State Oniver-	wiay 2012
• Member Phi Kanna Phi	April 2012
• Mathematical and Physical Sciences division at the California State Univer-	February 2012
sity Long Beach Student Research Competition [Local] (1 st place \$100)	rebruary 2012
• Kennedy Reed Award for Best Theoretical Research by a Graduate Student	October 2011
(1 st place, \$250) [American Physical Society California-Nevada Section 2011	
Annual Meeting]	
• Member American Physical Society (APS)	September 2011
• California State University, Long Beach Graduate Research Fellowship (1	2011-2012
of 2 awarded for the College of Science and Mathematics, \$9,000)	
• Phillip J. Ord Scholarship (1 of 2 awarded in the CSULB Department of	Fall 2011
Physics & Astronomy, \$1,000)	

• CSULB Physics & Astronomy Department Commendation for Teaching	Spring 2011
Excellence (1 of 4)	
• CSULB Physics & Astronomy Department Commendation for New Teach-	Spring 2010
ing Assistants (1 of 5)	
• Eagle Scout, Boy Scouts of America (Order of the Arrow)	Class of 2005
• Degree of Distinction, National Forensics League (Speech and Debate,	December 2004
Merit #1132635)	

TEACHING EXPERIENCE

Chemistry 252 Density Functional Theory	Fall 2016
University of California, Irvine	Irvine, California
Physics 50 Introduction to Mathematical Methods	Spring 2013
University of California, Irvine	Irvine, California
Physics 3A Basic Physics 1	Spring 2013
University of California, Irvine	Irvine, California
Physics 2 Math Methods	Fall 2011–Winter 2012
University of California, Irvine	Irvine, California
Graduate Electricity & Magnetism Grader	Spring 2012
California State University, Long Beach	Long Beach, California
Graduate Statistical Physics Grader	Spring 2012
California State University, Long Beach	Long Beach, California
Graduate Quantum Mechanics II Grader	Spring 2012
California State University, Long Beach	Long Beach, California
Graduate Math Methods Grader	Fall 2011
California State University, Long Beach	Long Beach, California
Graduate Classical Mechanics Grader	Fall 2011
California State University, Long Beach	Long Beach, California

Graduate Quantum Mechanics I Grader California State University, Long Beach Fall 2011 Long Beach, California **Instruction Facilitator** California State University, Long Beach

Introductory Labs (100A & 100B) California State University, Long Beach

Department and Private Tutor California Polytechnic State University, San Luis Obispo

Introductory Physics 1 & 2 Grader California Polytechnic State University, San Luis Obispo

Modern Physics Grader California Polytechnic State University, San Luis Obispo

Modern Physics Grader California Polytechnic State University, San Luis Obispo

PROFESSIONAL ACTIVITIES

Physics Graduate Caucus: Organizing Committee	2016-2017
Helped to craft a policy platform and organize the 2016 departmental hol-	
iday party. Organized the 2017 post-qualification exam social event.	
UC Irvine Science Communications Initiative: Science Communication	2016-2017
Internship	
Writing internship for the Loh Down on Science (ten manuscripts). Gave	
two instruction talks on writing scripts for public audiences.	
ITensor Developer	2015-2017
Developing tutorials and code for ITensor with E. Miles Stoudenmire.	
Travel support for seminar on ITensor from the Perimeter Institute for Theo-	
retical Physics in Waterloo, Canada.	
Simons Foundation Affiliated Scientist	2014-2017
Many Electron Collaboration with Steven R. White.	
American Physical Society Far West Section Student Representative	2014-2015
Elected to a one year term. Helped run and judge 2015 and 2016 Far West	
meeting.	
Possarch Crown Managar	2012 2014
Research Group Manager	2013-2010

Spring 2010 Long Beach, California

Spring 2009-2011 Long Beach, California

2007-2009 San Luis Obispo, California

2006-2007 San Luis Obispo, California

2006-2007 San Luis Obispo, California

2006-2007 San Luis Obispo, California

Managing all administrative and website duties in the group of Kieron Burke, wrote a Burke Diary, wrote a rule book 'The Tao of Kieron' for new students entering the group.	
UC Irvine Chemistry Alumni Newsletter Editor Edited the Fall 2013, Summer 2014, and Spring 2015.	2013-2015
Undergraduate Research Supervisor for Ovidiu E. Icreverzi Supervised Ovidiu E. Icreverzi leading to two publications.	Summer 2011
OUTREACH	
High School Mentoring Workshop (Hosted by A. Holmes) Irvine, CA, USA [Advising physicist: T.E. Baker]	June 2017
Cal Poly, San Luis Obispo Physics Department Colloquium (Hosted by J. Klay) San Luis Obispo, CA, USA <i>Being a Physicist</i> [Presentation: T.E. Baker]	May 2017
Molecular Biology 220: Science Communication Skills , Irvine, CA, USA <i>The Down Loh on the Loh Down on Science Writing</i> [Presentation: T.E. Baker]	April 2017
Loh Down on Science: New member meeting , Irvine, CA, USA <i>The Down Loh on the Loh Down on Science Writing</i> [Presentation: T.E. Baker]	April 2017
Grad Slam! Competition , Irvine, CA, USA <i>New particles with old materials: How neutrinos oscillate</i> [Presentation: T.E. Baker]	March 2017
The Machines Learn Physics 2017 March APS Meeting Press Highlights, New Orleans, USA <i>The Machines Learn Physics</i> [Presentation: T.E. Baker]	March 2017
Brews and Brains , Irvine, CA, USA <i>The Machines Learn Physics</i> [Presentation: T.E. Baker]	February 2017
Friday Pizza Talk (Hosted by the Physics Graduate Caucus), Irvine, CA, USA	January 2017

Superconducting-magnetic proximity systems [Presentation: T.E. Baker]

GPS-BIOMED Elevator Pitch Competition , Irvine, CA, USA [Presentation: T.E. Baker]	November 2016	
Activate to Captivate, Irvine, CA, USA [Presentation: T.E. Baker]	November 2016	
Molecular Biology 220 Presentation (taught by Sandra Tsing Loh), Irvine, CA, USA <i>The machines learn physics</i> [Video Presentation: T.E. Baker]	June 2016	
Friday Pizza Talk , Irvine, CA, USA <i>My Research in Condensed Matter Theory</i> [Presentation: T.E. Baker]	April 2016	
ARCS Foundation: 16 th Annual Scholar Awards Dinner , Irvine, CA, USA <i>How neutrinos oscillate (with superconductors)</i> [Presentation: T.E. Baker]	March 2016	
Prospective Student Presentations, Irvine, CA, USA Reproducing sterile neutrinos and the behavior of flavor oscillations with superconducting-magnetic proximity effects [Poster: T.E. Baker] Recruited students during prospective student tours hosted by the UCI Sigma Xi Chapter. Winner: Best poster	March 2016	
Pizza Talk: Kieron Burke , Irvine, CA, USA Where Density Functional Theory Meets Density Matrix Renormalization Group [Mini-Presentation by T.E. Baker]	October 2015	
GRE Boot Camp , Long Beach, CA, USA Studying for the Physics GRE: It's not about the physics [Presentation: T.E. Baker] Facilitated a GRE study session for underrepresented students in physics. Or- ganized by Professor P. Jaikumar.	August 2015	
Prospective Student Presentations , Irvine, CA, USA <i>Low Cost Mimicry of the Soft-Coulomb with Exponential Interactions</i> [Poster: T.E. Baker] Recruited students during prospective student tours hosted by the UCI Sigma Xi Chapter. Winner: Best poster	March 2015	

ARCS Foundation: 15th Annual Scholar Awards Dinner Irvine, CA, USA <i>Low Cost Mimicry of the Soft-Coulomb with Exponential Interactions</i> [Poster: T.E. Baker, E.M. Stoudenmire, L.O. Wagner, K. Burke, S.R. White]	March 2015
What is Graduate School All About Irvine, CA, USA [Panel Discussion: T.E. Baker] Advised students at CSUs interested in doing astrophysics at UC graduate schools as organized through the Cal-Bridge program from the National Sci- ence Foundation. Organized by Professor T. Smecker-Hane.	March 2015
Life After the Degree Long Beach, CA, USA [Panel Discussion: T.E. Baker] Advised underrepresented students in physics on career expectations at CSU Long Beach. Organized by Professor C. Kwon.	February 2015
GRE Boot Camp Long Beach, CA, USA <i>From the Master to the Doctor: A One Dimensional Journey</i> [Presentation: T.E. Baker] Facilitated a GRE study session for underrepresented students in physics. Or- ganized by Professor P. Jaikumar.	August 2014
GRE Boot Camp Long Beach, CA, USA <i>The Bead on a Hoop and Ferromagnetism: An Analogy Between Classical</i> <i>Mechanics and Magnetism</i> [Presentation: T.E. Baker] Facilitated a GRE study session for underrepresented students in physics. Or- ganized by Professor A. Bill.	May 2013
PhysTEC: Student Panel Long Beach, CA, USA [Panel Discussion: T.E. Baker] General discussion about university physics for high school students. Orga- nized by Professor G. Pickett.	April 2012
California State University, Long Beach Astronomy Outreach Long Beach, CA Operating, assisting, and managing undergraduate telescope time for astron- omy labs with Professor P. Hintzen and Dr. M. Frey.	2011-2012

PRESS

American Institute of Physics Mining Computer Simulations For New Ma-	April 2017
terials	
Physics World <i>APS</i> sees friction as fracture, cat pictures and brain implants	March 2017
ARCS President pH: Scholar Highlight	April 1, 2015
This Week @ The Beach: Cal State Long Beach Graduate, Undergraduate	May 21, 2012
Students Win Top Awards at 26th Annual CSU Statewide Student Research	
Competition	
Indiana Gazette: A Matter of Physics	May 19, 2012

MISCELLANEOUS

COMPUTER PROGRAMS	Fortran 90	julia	OpenMP	slurm/pbs	unix
& LANGUAGES	C++11	Mathematica	ITensor/Block	markdown	IAT _E X

ABSTRACT OF THE DISSERTATION

Methods of Calculation with the Exact Density Functional using the Renormalization Group

By

Thomas Edward Baker

Doctor of Philosophy in Physics University of California, Irvine, 2017

Professor Kieron Burke, Chair

Solving Schrödinger's equation is extremely important to determine the quantum mechanical properties of a material and model chemistry computationally. Density functional theory is one of the best scaling methods for large numbers of particles and can be used as a tool to investigate large quantum systems, but this method requires approximation in practice, leading to approximate answers. The exact density functional theory is still useful for investigation, despite not having the exact universal functional for all cases so the theory can be better understood. Here, we analyze the properties of the exact theory by accessing the exact functional. We do so by constructing a situation where this is possible: in one dimension with the aid of the density matrix renormalization group and machine learning techniques. This toolset is used to study the properties of the convergence of the exact functional. Important for any technique is how the problem is phrased in a particular basis, and we combine the methods of the renormalization group, through a family of transformations called wavelets, with density functional calculations to determine an optimized basis set with wavelets for a given quantum computation.

Chapter 1

Introduction

Quantum mechanics, as a predictive tool, is highly accurate. Even if the implications or physical description of the quantum phenomenon is questioned by some, the practical results of this should be trusted with a high confidence. While there exist some anomalous results that remain to be explained, practical application of quantum theory has produced a deep understanding of materials and many other (sometimes exotic) phenomenon. For example, if one wishes to snap a metal in half, it is important to understand how the bonds holding the individual atoms together at the molecular level will break. This understanding can lead to stronger materials or better conductors, to name only a tiny fraction of the possible applications of the theory.

When applied to the prediction of the solid state, solution of the eigenvalue problem suffers from the problem of many bodies. A material commonly encountered in the real world–perhaps a fork or a geode–contains Avogadro's number of electrons. Once it is established that these structures are periodic, however, calculations only on the primitive cell need be considered. Or in other situations such as a gas, computation on single molecules need be considered. Yet, this can still contain many, many electrons in cases of practical interest. Forcing computation on more than even ten electrons can easily surpass the computational resources that are available. This complexity extends from representing the system with the wavefunction, as it contains three coordinates for each electron.

Clearly, more clever approaches are required to obtain the properties of a quantum system.

Density functional theory is a way to reduce the amount of information that needs to be accounted for to describe the entirety of the many-body state. The single particle density was shown to be a sufficient to characterize a quantum system by Hohenberg and Kohn [1] and it contains only three coordinates for all electrons. The issue is that the proof showing that Schrödinger's equation can be rewritten into a form that only depends on the density is not constructive, we only know of its existence.

We know one more fact about the density functional which increases its usefulness. It is composed of two pieces. The first has a closed form and characterizes the external potential energy of a given system, though changing with each system. The second term is known as the universal functional and is independent of the external potential; however, this functional is not known. The universality of the density functional means that deriving an expression should give us access to any system, provided we adjust the external potential functional correctly. In practice, this introduces errors that can result in incorrect physics. Hence, it is possible to compute very efficiently with the density at the cost of obtaining an incorrect, though not necessarily inexact, answer with an approximation. The development of functionals can take decades before suitably improved semi-local density functionals are constructed from exact statements. This could be a never-ending endeavor since determining the exact universal density functional probably resides in a practically impossible regime of computational complexity [2]. Further, some recent mathematical developments have shed light on whether any method, or whether there *can be* any method, that solves any proposed quantum system. The answer is proven no as seen from implementing the halting problem into the quantum problem [3].

Not all hope is lost. Another, more realistic question can be asked: can a method, or functional, be found so that any realistic system of interest can be found to chemical accuracy? In other words,

can we get close enough for practical use?

The current work is focused on this question and also what can be found from from exact theory.

With many tens of thousands of papers published with density functional methods, it is more critical than ever to understand exact elements of the theory so we know where functional approximations fail and where they must be improved. It is still very difficult to advance density funcitonal theory from this route of exact statements and semi-local functionals, we can learn much about the exact density functional from studies where it is feasibly used, namely in one dimension. Highly accurate solvers in one dimension can be used to extract properties of exact density functional theory (*i.e.*, exact Kohn-Sham potentials, etc.). These would be inaccessible in higher dimensions due to the computational cost of inverting the exact density functional.

In this thesis, a complete understsanding of the exact functional for the given problem is obtained. We investigate the exact properties of the universal density functional with renormalization group methods. Principally, we use the density matrix renormalization group in order to provide exact answers in one dimension. In this setting, behaviors and features are more easily identifiable. The fundamental theorems of density functional theory still apply in different dimensions and for different interactions.

Chapter 2 was authored with E. Miles Stoudenmire and Lucas O. Wagner and details a onedimensional system that has some of the same behaviors of real chemical systems. It is used to generate results in the following chapters. The system is based on a spherically averaged interaction in one dimension, uses the density matrix renormalization group for exact computation, and derives a local density approximation for the exponential interaction. Chapter 3 was co-authored with Li Li and uses kernel ridge regression to machine learn the exact density functional from density matrix renormalization group results. Chapter 5 was co-authored with Lucas O. Wagner and E. Miles Stoudenmire and studies the convergence of the exact density functional. Chapter 4 generates an optimized basis set from an approximate calculation using wavelet transformations. This basis set obtains answers to chemical accuracy with a minimal number of functions in one dimension. Chapter 6 ends with a brief conclusion of the results of the work.

Two appendices were written as a part of the *Putting the Theory Back in Density Functional Theory* summer school at the Institute of Pure and Applied Mathematics. Appendix A was authored with Professor Carlos Cervera of the University of California, Santa Barbara on the mathematical specifics of the quantum many body problem, specifically following the arguments by von Neumann using self-adjoint operators. Appendix B was authored with Professor John Perdew of the Temple University on the history of the generalized gradient approximation. Note that variable assignments are different for each chapter.

Chapter 2

One Dimensional Mimicking of Electronic Structure: The Case for Exponentials

2.1 Overview

Efficient computation with quantum mechanics can be achieved with density functional methods. In order to explore these methods, it is important to examine them in a situation where the exact theory can be examined. That is, a one dimensional Hubbard model with enough sites to appear as a continuum. In this chapter, we generate an approximate density functional (the local density approximation) using the density matrix renormalization group and compare exact and approximate theories. This system will be used in the following chapters.

An exponential interaction is constructed so that one-dimensional atoms and chains of atoms mimic the general behavior of their three-dimensional counterparts. Relative to the more commonly used soft-Coulomb interaction, the exponential greatly diminishes the computational time needed for calculating highly accurate quantities with the density matrix renormalization group. This is due to the use of a small matrix product operator and to exponentially vanishing tails. Furthermore, its more rapid decay closely mimics the screened Coulomb interaction in three dimensions. Choosing parameters to best match earlier calculations, we report results for the one dimensional hydrogen atom, uniform gas, and small atoms and molecules both exactly and in the local density approximation.

This work was published with E. Miles Stoudenmire, Lucas O. Wagner, Kieron Burke, and Steven R. White and is republished here with permission from the American Physical Society [4].

2.2 Introduction

The notion that a strong electromagnetic field can be modeled well by a one dimensional (1d) problem dates back to at least 1939 when a calculation by Schiff and Snyder [5] assigned a potential in the *x* direction and "integrated out" the transverse degrees of freedom in the *y* and *z* directions by averaging over radial wave functions. The resulting interaction has been studied by several others [6, 7, 8, 9, 10, 11] including one work by Elliott and Loudon [6] that approximated the 1d potential, so it can be solved more easily.

Today, the most common approximation for the 1d potentials in a strong electromagnetic field was introduced by Eberly, Su, and Javaninen [12] who rewrote the Coulomb interaction $1/\sqrt{x^2 + y^2 + z^2}$ as $1/\sqrt{x^2 + a^2}$; the *x* component is allowed to vary independently and the remaining radial term in cylindrical coordinates, *a*, is set to a constant which is determined on a system-by-system basis for the particular application of study to match the ionization energy. This soft-Coulomb interaction has been used in a wide variety of applications requiring a 1d potential [12, 13, 14, 15, 16, 17, 18, 19, 20]. It has many attractive features including the avoidance of the singularity at zero separation while retaining a Rydberg series of excitations [21, 22, 23]. Even when not considering a strong electromagnetic field, the soft-Coulomb interaction has become the choice potential for 1d model systems.

A general use of 1d systems is as a computational laboratory for studying the limitations of electronic structure methods, such as density functional theory (DFT) [8, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38]. A key requirement is that the accuracy of such methods be at least qualitatively similar to their three dimensional (3d) counterparts. Helbig, et. al. [33] had already calculated the energy of the uniform electron gas with a soft-Coulomb repulsion, making the construction of the local density approximation (LDA) simple. Recently, some of us [35] used Ref. [33] to construct benchmark systems with the soft-Coulomb interaction which we used to study DFT approximations [1, 39, 40, 41]. It was also shown that the model 1d systems closely mimic 3d systems, particularly those with high symmetry. The 1d nature of these systems allows us to use the density matrix renormalization group (DMRG) [42] to obtain ground states to numerical precision. DMRG has no sign problem and works well even for strongly correlated 1d systems [43]. We also apply various DFT approximations to these systems in order to understand how such approximations could be improved, especially when correlations are strong. We have found that our 1d "pseudomolecules" closely mimic the behavior of real 3d molecules in terms of the relative size and type of correlations and also the errors made by DFT approximations [35]. Conclusions can be drawn from the 1d systems that are relevant to realistic 3d systems, a key advantage over lattice based models. Crucially, in 1d, we can extrapolate to the thermodynamic limit with far less computational cost compared to a similar calculation in 3d [44].

However, the soft-Coulomb interaction has some drawbacks as a mimic for 3d electronic structure calculations. First, the long 1/|x| tail has a bigger effect in 1d than in 3d, making the interaction excessively long ranged. Second, in 3d, the electron-electron interaction induces weak cusps as $\mathbf{r} \rightarrow 0$; the soft-Coulomb induces no cusps at all. While this can be a significant computational advantage with some methods, this precludes using it to study cusp behavior. Third, although the extra cost for treating power-law decaying interactions within DMRG can be made to scale sub-linearly with system size (via a clever fitting approximation [45, 46]), this cost is still much higher than for a system with strictly local interactions, for example, the Hubbard model [47].
As an alternative and complement to the soft-Coulomb interaction, we suggest an exponential interaction that addresses each of these weaknesses but whose parameters are chosen to give very similar results. Its tails are weaker, simulating the shorter ranged nature of the Coulomb interaction in 3d if screening is taken into account. The presence of a cusp in the potential more accurately reflects 3d calculations, since a discontinuity in the wavefunction or its derivatives may make convergence more difficult. Finally, the cost for using exponential interactions within DMRG is no more than for using local interactions; in practice this makes DMRG calculations with exponential interactions to the thermodynamic and continuum limits with exponential interactions also require less computational time.

The primary purpose of this paper is therefore to show in what ways an exponential interaction is preferable to the soft-Coulomb interaction in 1d electronic structure calculations and to provide reference results for such systems. Showing that the soft-Coulomb interaction is well approximated by the exponential would allow for the efficient and fast use of DMRG over QMC methods for 1d systems, so we construct our exponential to also mimic 1d soft-Coulomb calculations and allow for comparison with previous results [31, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61].¹

We derive some general analytic forms for the exponential hydrogenic atom in Sec. 2.3 and discuss mimicking the soft-Coulomb interaction with a = 1 in Sec. 2.3.2. Section 2.4 summarizes the numerical tools used to find accurate results of the exponential systems. We find the uniform gas energies with DMRG and derive high and low density asymptotic limits in Sec. 2.5. Finite system calculations and benchmarks for the soft-Coulomb-like exponential interaction are given in Sec. 2.6. The Supplemental Material contains all necessary raw data to reproduce results [4].

¹Notes by L. Balents for K. Burke.

2.3 Hydrogenic Atoms

2.3.1 General Analytic Expressions

We wish to solve the 1d exponential Hydrogenic atom, with the potential:

$$v_{\rm en}(x) = -Zv_{\rm exp}(x), \quad v_{\rm exp}(x) = A\exp(-\kappa|x|). \tag{2.1}$$

where *A* and κ characterize the interaction and *Z* is the 'charge' felt by an electron (e) from a nucleus (n). Since the potential is even in *x*, the eigenstates will be even and odd, and we label them i = 0, 1, 2... (alternating even to odd). Writing

$$z(x) = (2\sqrt{2AZ}/\kappa) \exp(-\kappa x/2), \quad x \ge 0,$$
(2.2)

the Schrödinger equation becomes the Bessel equation. The wavefunction solution is a linear combination of $J_{\pm \nu}(z)$, where $\nu^2 = -8E/\kappa^2$, and J is a Bessel function of the first kind. The negative index $(-\nu)$ functions diverge as $x \to \infty$, so the wavefunction is proportional to $J_{\nu}(z)$ and the density is

$$n(x) = C^2 J_{\nu}^2(z(|x|)) \tag{2.3}$$

where *C* is chosen so that $\int dx n(x) = 1$.

The eigenvalues, E, are determined by spatial symmetry, so that:

$$\frac{d}{dx}J_{\nu}(z)\Big|_{z_0} = 0 \text{ (even)}, \quad J_{\nu}(z_0) = 0 \text{ (odd)},$$
 (2.4)

with $z_0 = z(0)$. This condition implies that the eigenfunctions are Bessel functions of non-integer index. Defining $j'_i(v)$ and $j_i(v)$ to be zeroes of these functions, indexed in order (see e.g., Ref.

[62], Sec 9.5), the energy eigenvalues are

$$E_i = -\kappa^2 v_i^2(z_0)/8, \quad i = 0, 1, 2, \dots$$
(2.5)

where $v_i(z_0)$ satisfies

$$j'_{i+1}(\mathbf{v}_{2i}) = z_0, \quad j_i(\mathbf{v}_{2i-1}) = z_0.$$
 (2.6)

We found no source where these are generally listed or approximated but they are available in, e.g., Mathematica. One can deduce the critical values of z_0 at which the number of bound states changes (when E = 0), since $j'_1(0) = 0$, $j'_2(0) = 3.83171$, $j'_3(0) = 7.01559$, and $j_1(0) = 2.40483$ and $j_2(0) = 5.52008$ (Table 9.5 of Ref. [62]).

Unlike a soft-Coulomb potential, cusps appear for the exponential in analogy with 3d Coulomb systems. Rewriting the Schrödinger equation as $\psi''/(2\psi) = v_{en}(x) + E$, where ψ is the ground state wavefunction and primes denote derivatives, shows this ratio contains the cusp of the potential at the origin.

2.3.2 Mimicking Soft-Coulomb Interactions

Now we choose the parameters of our exponential to match closely those of the soft-Coulomb we have previously used in these studies, which has softness parameter a = 1. In that case, the ground-state energy of the 1d H atom is -0.669778 to μ Ha accuracy [12, 35],² and the width of the ground state density, $\int dx n(x)x^2$, is 1.191612. We find A and κ of $v_{\exp}(x)$ to match these values, yielding:

$$A = 1.071295$$
 and $\kappa^{-1} = 2.385345.$ (2.7)

²References [35] and [12] gives the ground state energy as -0.669777, but a truncation in the variables A and κ change our energy slightly.



Figure 2.1: An exponential interaction with A = 1.071295 and $\kappa^{-1} = 2.385345$ mimics the soft-Coulomb (a = 1) hydrogen ground-state density very closely.

Figure 2.1 shows the close agreement between the soft-Coulomb and the exponential in both the potential and the density for the 1d H atom. Hereafter, we take these values as defining our choice of exponential interaction.

These values for our hydrogen atom yield $z_0 = 6.983117$, so that it binds exactly four states. Since z_0 is proportional to \sqrt{Z} , where Z is the nuclear charge for a hydrogenic atom, a fifth state is just barely bound when Z = 1.00931. This is a marked difference from the non-interacting soft-Coulomb [63] and non-interacting 3d hydrogen [64] atoms which each bind an infinite number of states.

We then choose the repulsion between electrons to be the same but with opposite sign:

$$v_{\rm ee}(x-x') = v_{\rm exp}(x-x').$$
 (2.8)

Solutions for more than one electron are remarkably similar to the soft-Coulomb under these conditions. For example, both the soft-Coulomb and the exponential bind neutral atoms only up to Z = 4. We further note that H⁻ is bound, but H⁻⁻ is not, for all three cases (exponential, soft-Coulomb, and reality).

2.4 Calculational Details and Notation

DMRG is an exceedingly efficient method for calculating low-energy properties of 1d systems and gives variational energies. For the types of systems considered here, DMRG is able to determine essentially the exact ground state wavefunction [43, 46]. DMRG works by iteratively determining the minimal basis of many-body states needed to represent the ground state wavefunction to a given accuracy. For 1d systems, one can reach excellent accuracy by retaining only a few hundred states in the basis. The basis states are gradually improved by projecting the Hamiltonian into the current basis on all but a few lattice sites, then computing the ground state of this partially

projected Hamiltonian. The new trial ground state is typically closer to the exact one, making it possible to compute an improved basis.

Our calculations are done in real space on a grid.³ The grid Hamiltonian is chosen to be the extended Hubbard-like model also used in Ref. [35] (see Eq. (3) of that work). The electronelectron interaction and external potentials are changed to the exponentials used here. Note that the convention we use to evaluate integrals is to multiply the value of the integrand at each grid point by the grid spacing to match Ref. [35]. So, for here,

$$\int dx f(x) \approx \Delta \sum_{i} f(x_{i})$$
(2.9)

for some function f(x) and grid spacing Δ . Grid points are indexed by *i* and span the interval of integration.

Using an exponential interaction within DMRG is very natural since it can be exactly represented by a matrix product operator, the form of the Hamiltonian used in newer DMRG codes [45]. In fact, the soft-Coulomb interaction used in Ref. [35] was actually represented by fitting it to approximately 25 exponentials [65].

The majority of our focus is on finite systems and we use a finite grid with end points chosen to make the wavefunction negligible. For chains, we place the ends of the grid at the first missing nucleus, although in the case of a single atom or isolated molecule, we will place the boundary sufficiently far from the nuclei to avoid noticeable effects. This can be much nearer to the nuclei than in the soft-Coulomb systems. We always use the convention of placing a grid point on a cusp when possible, to avoid missing any kinetic energy.

In Kohn-Sham (KS) DFT [39], we use density functionals which are defined on the KS system, a non-interacting system that has the same density and energy as the full interacting system. Although, this non-interacting system has a different potential, $v_s(x)$, the KS potential. The ground

³Calculations were performed using the ITensor Library: http://itensor.org/

state energy, E, of an interacting electron system is the sum of the kinetic energy, T, the electronelectron repulsion, V_{ee} , and the one-body potential energy, V. The ground state energy, E, is the minimization in n of the density functional

$$E[n] = T_{\rm s}[n] + U[n] + V[n] + E_{\rm xc}[n], \qquad (2.10)$$

where

$$T_{\rm S}[n] = \frac{1}{2} \sum_{\sigma} \sum_{i=1}^{N_{\sigma}} \int dx \left| \frac{d}{dx} \phi_{i,\sigma}(x) \right|^2 \tag{2.11}$$

is the non-interacting kinetic energy evaluated on the occupied non-interacting KS orbitals, $\phi_{i,\sigma}$, for N_{σ} particles of spin σ . The difference, $T_{\rm C} = T - T_{\rm S}$, gives the difference between the interacting and non-interacting kinetic energy. The Hartree integral is defined as

$$U[n] = \frac{1}{2} \iint dx dx' v_{ee}(x - x') n(x) n(x').$$
(2.12)

The one-body potential functional is

$$V[n] = \int dx v(x) n(x), \qquad (2.13)$$

where v(x) is the attraction to the nuclei. Equation 2.10 defines the exchange-correlation (XC) functional, $E_{\rm XC}[n]$, which is the sum of the exchange (X) and correlation (C) energies. The exchange energy can be evaluated over the occupied KS orbitals as

$$E_{\rm X}[n] = -\frac{1}{2} \sum_{\sigma} \sum_{i,j=1}^{N_{\sigma}} \int dx \int dx' v_{\rm ee}(x-x') \phi_{i,\sigma}^*(x) \phi_{j,\sigma}^*(x) \phi_{i,\sigma}(x') \phi_{j,\sigma}(x'), \qquad (2.14)$$

but in practice it is often approximted by an explicity density functional to reduce the computational cost.

2.5 Uniform Gas

In order to construct and employ the LDA for our exponential repulsion, we must first calculate the exchange-correlation energy of the exponentially repelling uniform gas, expellium.

2.5.1 Kinetic, Hartree, and Exchange Energies

These energy components are straightforward and well known, as the single particle states are simply plane waves. The unpolarized, non-interacting kinetic energy per length of a uniform gas is given by [66, 67, 68]

$$t_{\rm S}^{\rm unpol}(n) = \pi^2 n^3 / 24.$$
 (2.15)

The Hartree energy per length of a uniform system with exponential interaction is finite:

$$eH^{\text{unif}}(n) = A n^2 / \kappa. \tag{2.16}$$

The exchange energy of the uniform gas was derived in Ref. [69], with the energy per length as

$$e_{\rm X}^{\rm unpol}(n) = A\kappa \left(\ln(1+y^2) - 2y \arctan y \right) / (2\pi^2)$$
 (2.17)

where $y = \pi/(2\kappa r_s)$ where r_s is the Wigner-Seitz radius [70] in 1d defined as $r_s = 1/(2n)$ [71]. The limits for this expression are

$$e_{\rm X}^{\rm unpol}(n) \to -An/2, \qquad n \to \infty$$
 (2.18)

 $e_{\rm X}^{\rm unpol}(n) \rightarrow -An^2/(2\kappa), \qquad n \rightarrow 0.$ (2.19)

Both the exchange and kinetic energies depend separately on the orbitals of each spin, so they satisfy simple spin scaling relation [72]:

$$E_{\rm X}[n,\zeta] = \frac{1}{2} \left\{ E_{\rm X}^{\rm unpol}[(1+\zeta)n] + E_{\rm X}^{\rm unpol}[(1-\zeta)n] \right\}$$
(2.20)

where $\zeta(x) = (n_{\uparrow}(x) - n_{\downarrow}(x))/n(x)$ is the local spin polarization for spin up (down) densities n_{\uparrow} (n_{\downarrow}). Applying the relation for $T_{\rm s}$ yields:

$$t_{\rm s}^{\rm unif}(n,\zeta) = t_{\rm s}^{\rm unpol}(n)(1+3\zeta^2)/2$$
(2.21)

and the exchange energy per length:

$$e_{\mathbf{X}}^{\mathrm{unif}}(n,\zeta) = \sum_{\sigma=\pm 1} e_{\mathbf{X}}^{\mathrm{unpol}} \left((1+\sigma\zeta)n \right) / 2.$$
(2.22)

In Fig. 2.2, we plot the exchange energies per unit length for both the unpolarized and fully polarized cases, comparing with the soft-Coulomb. For $r_{\rm s} \leq 2$, *i.e.* $n \gtrsim 1/4$, they are very similar, but the exponential vanishes more rapidly in the low density limit. Applying Eq. (2.19) to Eq. (2.22) shows $e_{\rm x}^{\rm unif}$ is independent of ζ in the high-density limit. Application of Eq. (2.18) shows $e_{\rm x}^{\rm unif}(n,\zeta) \rightarrow e_{\rm x}^{\rm unpol}(n)(1+\zeta^2)$ as $n \rightarrow 0$.

2.5.2 Correlation Energy

While we can determine the exchange energy of the uniform gas analytically, for correlation we cannot. We first determine the high and low density limits and connect them with a Padé approximation.



Figure 2.2: Exchange energy densities per particle of the uniform gas for the exponential (solid lines), both unpolarized (blue) and fully polarized (red). Dashed lines show soft-Coulomb results.

2.5.3 High Density Limit

In the high-density uniform gas, the RPA solution becomes exact [73, 74, 75, 76, 77, 78, 78, 79, 80, 81, 82]. Casula, *et. al.* [11] have derived a criteria for the RPA limit which for 1d systems gives $E_{\rm C} = -\Upsilon r_{\rm S}/\pi^4$ where $\Upsilon = \int_0^\infty dq \, q \tilde{v}_{\rm ee}^2(q)$ for the Fourier transform, $\tilde{v}_{\rm ee}(q) = 2A\kappa/(\kappa^2 + q^2)$ [9, 10, 11, 33]. Thus,

$$E_{\rm C}^{\rm RPA}(n) = \begin{cases} -2A^2 r_s / \pi^4 & \text{unpolarized,} \\ -A^2 r_s / (4\pi^4) & \text{polarized.} \end{cases}$$
(2.23)

Note that these expressions for the exponential $e_{\rm C}^{\rm RPA}$ are identical to the $e_{\rm C}^{\rm RPA}$ of the soft-Coulomb interaction if A = 1 and so differ by less than 15% here [33].

2.5.4 Low Density Limit

To determine the low density limit of the correlation, we may work in the limit of a Wigner crystal [83]. This phase occurs because the kinetic energy becomes less than the interaction energy for low densities. The strictly correlated electron limit [29, 84, 85] is the exact limit of the low density electron gas [71, 86]. For strictly correlated electrons, each electron sits some multiple of $2r_s$ away from any other. For short-ranged interactions, such as the exponential, the potential energy must decay exponentially with r_s , so that $E_{xc} = -U$, regardless of spin polarization [72]. The actual form of the correlation energy E_c , however, will depend on the polarization, because the exchange energy e_x does. For a spin-unpolarized system, using Eq. (2.19), we find $e_x(n) = E_c(n) = -An^2/(2\kappa)$ in the low-density gas limit. After spin-scaling exchange, we obtain the low-density limit $e_x^{pol}(n) = -An^2/\kappa$, and this quantity already cancels the Hartree energy! Therefore the correlation energy for spin-polarized electrons must decay more rapidly than n^2 as $n \rightarrow 0$.



Figure 2.3: Correlation energy densities of the uniform gas from DMRG calculations. Solid lines are parametrization of Eq. (2.24), red dots are calculated, and dashed lines are for the soft-Coulomb.

2.5.5 Correlation Energy Calculations

The uniform gas correlation energy was found from a sequence of DMRG calculations in boxes of increasing length, *L*, in which the average density is kept fixed. Grid errors become more pronounced in these systems compared with soft-Coulomb interactions because there is no way to ensure a grid point will always lie on the wave function's cusp. Hence, a very fine grid spacing was necessary to converge the points. As the density increases, finer and finer grids were necessary, down to a practical limit of $\Delta = 0.008$. Energies for different box sizes were fit to a parabola in 1/L and the limit of $L \rightarrow \infty$ extracted. The various energy components of Sec. 2.5.1 were then subtracted to find E_c to make the dots in Fig. 2.3. For partially polarized gases, we used the same

	α	β	γ	δ	η	σ
$e_{\rm C}^{\rm unpol}$	2	-1.00077	6.26099	-11.9041	9.62614	-1.48334
$e_{\rm C}^{\rm pol}$	180.891	-541.124	651.615	-356.504	88.0733	-4.32708

Table 2.1: Fitting parameters for the correlation energy in Eq. (2.24). The parameter v = 1 (unpolarized) or 8 (polarized).

procedure as for the unpolarized case except that each box contained various values of ζ for each L used in the limit. Evaluating several partially polarized systems, we found that the correlation energy was very nearly parabolic in ζ at several different densities.

2.5.6 Padé Approximation

Considering the asymptotic limits of the correlation energy, the full approximation that allows us to accurately fit the data is

$$E_{\rm C}^{\rm unif} = \frac{-A\kappa y^2/\pi^2}{\alpha + \beta\sqrt{y} + \gamma y + \delta y^{3/2} + \eta y^2 + \sigma y^{5/2} + v \frac{\pi\kappa^2}{A} y^3}.$$
(2.24)

where y was defined above and the fitting parameters are defined for this specific choice of A and κ only. The parameters optimized by fitting DMRG uniform gas data are given in Table 2.1, and the resulting fits are shown in Fig. 2.3. Although we know at full polarization $E_{\rm C}$ should decay more rapidly than n^2 in the low density limit, we do not know how much more rapidly, so we use the same form as the unpolarized case. This fit is accurate and the coefficient of n^2 is about 1% that of the unpolarized one. Finally, we approximate the ζ dependence as

$$E_{\rm C}(n,\zeta) = E_{\rm C}^{\rm unpol}(n) + \zeta^2 \Big(E_{\rm C}^{\rm pol}(n) - E_{\rm C}^{\rm unpol}(n) \Big),$$
(2.25)

as justified in the previous section.

In Fig. 2.4, we show the combined XC energies (solid) for the unpolarized (blue) and polarized



Figure 2.4: XC energy per particle, $e_{\rm XC}/n$ (dashed), for the unpolarized (blue) and fully polarized (red). Solid lines are $e_{\rm X}/n$ only.

gases (red). Dashed lines are for exchange alone. Correlation is a much smaller effect in the fully spin-polarized gas.

2.6 Finite Systems

2.6.1 Atomic Energies

We now refer to several tables that contain the information from several different systems as determined by the methods of the previous sections. To construct the LDA, $E_{\rm XC}^{\rm LDA}$ is constructed from Eqs. (2.30) and (2.25). In practice, we always use spin-DFT, and the local spin density approximation (LSDA). The plot of $e_{\rm XC}^{\rm unif}(r_{\rm S}, \zeta)$ is very similar to those of the soft-Coulomb (see Fig. 2 of Ref. [35]).

Table 2.2 contains many energy components for all 1d atoms and ions up to Z = 4. The total energies are accurate to within 1 mHa. The first approximation in quantum chemistry is the Hartree-Fock (HF), and its error is the (quantum chemical) correlation energy, $E_{\rm C}^{\rm QC}$. As required, this is

Ne	Symb.	E ^{HF}	E	$E_{\rm C}^{\rm QC}$	T	V	Vee	Ts	U	E _{xc}	Ex	E _C	T _C	ELDA	$E_{\rm X}^{\rm LDA}$	$E_{\rm C}^{\rm LDA}$
1	Н	-0.670	-0.670	0	0.111	-0.781	0	0.111	0.345	-0.345	-0.345	0	0	-0.643	-0.305	-0.009
	He ⁺	-1.482	-1.482	0	0.190	-1.672	0	0.190	0.379	-0.379	-0.379	0	0	-1.449	-0.337	-0.007
	Li ⁺⁺	-2.334	-2.334	0	0.259	-2.593	0	0.259	0.397	-0.397	-0.397	0	0	-2.298	-0.355	-0.006
	Be ³⁺	-3.208	-3.208	0	0.321	-3.529	0	0.321	0.408	-0.408	-0.408	0	0	-3.171	-0.366	-0.005
2	H ⁻	-0.694	-0.737	-0.044	0.114	-1.311	0.460	0.081	1.070	-0.586	-0.535	-0.051	0.050	-0.711	-0.520	-0.073
	He	-2.223	-2.237	-0.014	0.286	-3.212	0.690	0.273	1.432	-0.730	-0.716	-0.014	0.013	-2.196	-0.633	-0.050
	Li ⁺	-3.884	-3.892	-0.008	0.433	-5.080	0.755	0.426	1.541	-0.779	-0.770	-0.009	0.007	-3.842	-0.686	-0.039
	Be ⁺⁺	-5.606	-5.611	-0.005	0.564	-6.967	0.792	0.559	1.602	-0.806	-0.801	-0.005	0.005	-5.556	-0.715	-0.034
3	Li	-4.199	-4.215	-0.016	0.628	-6.490	1.647	0.614	2.751	-1.089	-1.072	-0.017	0.014	-4.181	-0.999	-0.045
	Be ⁺	-6.447	-6.457	-0.010	0.910	-9.225	1.858	0.900	3.029	-1.161	-1.150	-0.011	0.010	-6.411	-1.074	-0.035
4	Be	-6.756	-6.809	-0.053	1.118	-11.115	3.188	1.077	4.710	-1.481	-1.421	-0.060	0.041	-6.784	-1.371	-0.080

Table 2.2: Energy components for several systems as calculated by DMRG to 1 mHa accuracy. Chemical symbols H, He, Li, and Be imply single atomic potentials of Z = 1,2,3, and 4, respectively. All LDA calculations are self-consistent, except H⁻, which is unbound, so we evaluate $E_{\rm xc}^{\rm LDA}$ on the exact density. These values are very similar to those of the soft-Coulomb.

always negative and is typically a very small fraction of |E|. Unlike real atoms and ions, for fixed particle number $N, E_{\rm C} \rightarrow 0$ as $Z \rightarrow \infty$, not a constant [87].

The next three columns show the breakdown of *E* into its various components. The magnitude of |V| is much greater than the other two. Unlike 3d Coulomb systems, there is no virial theorem relating *E* and -T, for example [88]. Here the kinetic energies are much smaller than |E|, just as for the soft-Coulomb [35]. In the following three columns we give the KS components of the energy. These were extracted by finding the exact $v_s(x)$ from n(x) [38], and constructing the exact KS quantities [39]. Unlike 3d Coulomb reality, T_s is smaller in magnitude than $|E_{xc}|$. But just like in 3d Coulomb reality, both T_s and E_{xc} always grow with *Z* if *N* is fixed, with *N* if *Z* is fixed, or with *Z* for Z = N [89].

The next set of columns break $E_{\rm XC}$ into its components: $E_{\rm X}$, $E_{\rm C}$, and $T_{\rm C}$. The correlation energy is negative everywhere and is slightly larger in magnitude than $|E_{\rm C}^{\rm QC}|$ as required [90]. We also see $T_{\rm C}$ is very close to $-E_{\rm C}$ everywhere, a sign of weak correlation [91], which is the same as in 3d Coulomb atoms and ions. We also report self-consistent LDA energies and the XC components. All LDA energies are insufficiently negative. For N = 1, self-interaction error occurs and $E_{\rm XC}^{\rm LDA}$ is not quite -U. Just as for reality, LDA exchange consistently underestimates the magnitude of $E_{\rm X}$, while $E_{\rm C}^{\rm LDA}$ overestimates, producing the well-known cancellation of errors in $E_{\rm XC}^{\rm LDA}$.

N _e	Symb.	LI	DA	H	Exact	
		$-\varepsilon H$	Ι	$-\varepsilon H$	Ι	$I = -\varepsilon H$
1	Η	0.412	0.643	0.670	0.670	0.670
2	H^{-}	-	0.062	0.058	0.024	0.068
	He	0.478	0.714	0.750	0.741	0.755
	Li ⁺	1.238	1.508	1.556	1.550	1.558
	Be ⁺⁺	2.061	2.348	2.402	2.403	2.403
3	Li	0.182	0.339	0.327	0.315	0.323
	Be ⁺	0.643	0.855	0.850	0.836	0.846
4	Be	0.183	0.373	0.327	0.309	0.331

Table 2.3: Highest occupied eigenvalues (εH) and total energy differences (*I*) for several atoms and ion, both exactly and approximately.

We close the section on atoms with details of eigenvalues. It is long known that [92], for the exact KS potential, the highest occupied eigenvalue is at -I, the ionization energy, but that this condition is violated by approximation. In Table 2.3, we list $-\varepsilon H$ and I for several atoms and ions exactly, in HF and in LDA. Koopman first argued [93] that $-\varepsilon H$ should be a good approximation to I in HF, and we see that, just as in reality, it is a better approximation to I than I^{HF} , from total energy differences. On the other hand, our 1d LDA exhibits the same well-known failure of real LDA: its KS potential is far too shallow, so that $\varepsilon H^{\text{LDA}}$ is above εH by a significant amount (up to 10 eV).

2.6.2 Molecular Dissociation

Next we consider 1d molecules with an exponential interaction. The behavior is almost identical to that of the soft-Coulomb documented in Ref. [35]. For H₂⁺, in Fig. 2.5, HF is exact, and $E_0^{\text{LSDA}}(R \rightarrow \infty)$ does not tend to $E_0^{\text{LSDA}}(H)$ because of a large self-interaction error [94].

For H₂, in Fig. 2.6, the exact curve is calculated with DMRG, which has no problems whatsoever with stretching the bond (and can even break triple bonds [95]). But HF, restricted to a singlet, tends to the wrong limit as $R \to \infty$, while unrestricted HF goes to a lower energy beyond the Coulson-Fischer [96] point (R = 2.1) and dissociates to the correct energy (2E(H)) but the wrong



Figure 2.5: Molecular dissociation for H_2^+ for LSDA and HF. Dashed lines indicate the energy of a single H atom. Results are in close agreement with the soft-Coulomb interaction. LSDA has the well known failure of not dissociating to the correct limit.



Figure 2.6: Molecular dissociation for H_2 with dots denoting the Coulson-Fischer points. Curves are shown for the exact case; also shown are restricted (solid) and unrestricted (dashed) LSDA and HF.

		H_2^+	H ₂				
quantity	LSDA	exact	HF	LSDA	exact		
$D_{\rm e}~({\rm eV})$	3.94	3.72	2.04	3.25	2.74		
R_0 (bohr)	2.70	2.50	1.45	1.60	1.56		
ω (×10 ³ cm ⁻¹)	2.03	2.32	3.91	3.52	3.40		

Table 2.4: Electronic well depth D_e (calculated relative to well-separated unrestricted atoms), equilibrium bond radius R_0 , and vibrational frequency ω for the H₂⁺ and H₂ molecules.

spin symmetry [97]. The same qualitative behavior occurs for LSDA at R = 3.5. These results are almost identical to those with soft-Coulomb interactions (except R = 3.4 for the soft-Coulomb LSDA Coulson-Fischer point), and qualitatively the same as 3D.

For reference purposes, we also report equilibrium properties of H₂ and H₂⁺ in Table 2.4. HF is exact for H₂⁺, but underbinds H₂, shortens its bond, and yields too large a vibrational frequency, just as in 3d. Overall, LSDA results are substantially more accurate. LSDA overbinds, yields slightly (to less than 1%) too large a bond, and only slightly overestimates vibrational frequencies, just as in reality. Vibrational frequencies, ω , are chosen to fit the function $E_0 + \omega^2 (r - R_0)^2/2$.

2.6.3 Relative Advantages

To illustrate the effective shorter range of the exponential relative to a soft-Coulomb, Fig. 2.7 shows the exact binding energy of two H₂ molecules (with bond lengths set to their equilibrium values for each type of interaction) as a function of the separation between closest nuclei. These closed shell molecules do not bind with either interaction, but the soft-Coulomb energy decays far more slowly to its value at ∞ .

Finally, we give an example of the much lower computational cost of the exponential in DMRG over that of the soft-Coulomb due to the reasons discussed in Sec. 4.2. In Fig. 2.8, we plot the densities and potentials for a 10-atom H chain with separations R = 2.8. The densities are sufficiently similar for all practical purposes (but not the potentials) while the computational time



Figure 2.7: Binding energy curves for two H₂ molecules a distance *R* apart (measured between the innermost atoms), demonstrating the much slower decay of the soft-Coulomb. We subtracted off the asymptote of the binding curve so that the curves tend to zero. The inset shows the soft-Coulomb potentials from the two H₂ atoms have a substantial overlap even at R = 18 while the exponential does not.



Figure 2.8: The density of an H_{10} chain with R = 2.8 with exponential and soft-Coulomb interactions.

per DMRG sweep was about 4 times longer for the soft-Coulomb. With increasing interatomic distance, Fig. 2.9 shows a decreased wall time of more than a factor of 20 for calculating larger separations.

2.7 Conclusion

We have introduced an exponential interaction that allows us to mimic many features of real electronic structure with 1d systems. Using the exponential in place of the more standard soft-Coulomb interaction not only improves the computational time of DMRG, but it also allows faster convergence for other calculations due to its fast decay and local nature. To facilitate comparison with existing calculations, we choose the parameters in the exponential to best match a soft-Coulomb potential. A parameterization for the LDA is given by calculating and fitting to uniform gas data.



Figure 2.9: The exponential performs sweeps in DMRG much faster, leading to a greatly reduced computational time. Here we show the cost of the H_{10} of Fig. 2.8 as a function of interatomic separation. The number of many body states is fixed at 30 for 10 sweeps and each system has 1161 grid points. The maximum truncation error in each sweep is $\sim 10^{-8}$.

2.8 Supplementary material: Construction of the Local Density Approximation

This section contains more information on the low and high density limits for the exchange and correlation energy derived cursorily in the above text.

In any Kohn-Sham calculation, the exchange-correlation energy, $E_{\rm XC}$, must be approximated. We will note that exact exchange may be determined from the following functional

$$E_{\rm X} = -\frac{1}{2} \sum_{\sigma} \sum_{i,j=1}^{N_{\sigma}} \int dx \int dx' v_{\rm ee}(x-x') \psi_{i\sigma}(x) \psi_{j\sigma}(x) \psi_{j\sigma}(x') \psi_{i\sigma}(x'). \qquad (2.26)$$

(where a spin sum over σ and occupied orbital sum over *i*, *j* is performed) but is often computationally expensive to use in a DFT calculation and may not induce a cancellation of errors that allows DFT to reach better accuracy as we do not have a closed form for exact correlation [?].

The next section will derive the LDA exchange which will greatly diminish the computational time necessary for the calculation of the exchange at only a tiny cost of accuracy. This will also allow a cancellation of errors with the eventual LDA correlation functional.

2.8.1 Exchange Energy

The exchange energy is known to satisfy exact sum rules in that the exchange hole, n_x , integrates to -1. By deriving the exact exchange hole in the local approximation, we can determine a closed form expression for the exchange energy. We do so to construct our LDA.

Since the exchange hole relates exactly to the single particle density matrix, $n_X(x,x') = -|\gamma_s(x,x')|/n(x)$, we may set about determining the single particle density matrix γ_s for the uniform gas containing plane wave eigenstates,

$$\gamma_{s}(x,x') = N \int dx_{2} \dots \int dx_{N} \psi^{*}(x,x_{2}\dots,x_{N})$$
$$\times \psi(x',x_{2}\dots,x_{N}) = \frac{\sin(k_{F}u)}{\pi u}$$
(2.27)

where we note that for the uniform gas, a neglected term dependent on x + x', measured from a coordinate system with its origin at the walls placed at $-\infty$, is a much larger number than the difference $u \equiv x - x'$. Since sinc *u* decays extremely quickly, only the term containing the difference *u* contributes to γ_s .

With the single particle density matrix and the density of the uniform gas being constant, we have the exchange energy as

$$E_{\rm X}[n] = \iint dx dx' A \exp(-\kappa |x-x'|) n(x) n_{\rm X}(x,x').$$
(2.28)

with

$$n_{\rm X}(x,x') = -\frac{n}{4} {\rm sinc}^2(k_F(x-x'))$$
(2.29)

The exchange energy for the uniform gas will diverge as it is an infinite system (and therefore the exchange of two particles, even in the non-interacting KS system, will require an infinite amount of energy at infinite distance). So, we may then instead focus on the energy density, $\varepsilon_{\rm X}(n,x)$, which relates as $E_{\rm X}[n] = \int \varepsilon_{\rm X}(n,x) dx$.

Performing the integration gives

$$\varepsilon_{\rm X}(n,x) = A\left(\frac{\ln(1+n^2\pi^2/\kappa^2)}{2\pi^2/\kappa} - \frac{n}{\pi}\arctan(n\pi/\kappa)\right).$$
(2.30)

This exchange energy captures the exchange energy of a Hartree-Fock calculation exactly proving its validity.

Having derived the exchange functional, we move onto the correlation functional.

2.8.2 Low Density Limit

To determine the low density limit of the correlation, one may notice that scaling the coordinates by a factor $\gamma(x \rightarrow \gamma x)$ shows that in the low density limit, the electron-electron interaction is greater than the kinetic energy,

$$\lim_{\gamma \to 0} T^{\gamma}[n] = \lim_{\gamma \to 0} \gamma^2 T[n] = 0 < \lim_{\gamma \to 0} V_{ee}^{\gamma}[n] = A.$$

$$(2.31)$$

Hence, the electron will localize as a Wigner crystal and the energy of this system will be primarily determined by the electrostatic interaction of the electrons with the positive background charge (which neutralizes the total charge of the system). Note that the broken translational symmetry phase very closely matches the energy of the uniform gas in the region. Implicitly, we include a positive uniform background and cancel the Hartree term which would produce an infinite energy for the exponentially interacting system otherwise.

In a Wigner crystal, which may occur for low, uniform densities n(x) = n of electrons that individually localize in a region from $x = -r_s$ to r_s where r_s is the Wigner-Seitz radius in one dimension defined as $2/r_s(x) = n(x)$ [71]. For the electrostatic energy, first consider the positive background charge which will have the same density as that of the electrons. Locally, the electrons will be attracted to the positive charge on the line from $-r_s$ to r_s . For an exponential interaction, the potential, $\Phi(x)$ produced by this uniform positive charge is

$$\Phi(x) = \int_{-r_s}^{r_s} dy n A \exp(-\kappa |x-y|) = r_s^{-1} [1 - \exp(-\kappa r_s) \cosh \kappa x].$$
(2.32)

From this potential, we can determine the relevant energies. A classical electron sitting in this potential will rest at x = 0 with energy $-\Phi(0)$. The background charge interacts with itself with energy, $V_{\rm b}$,

$$V_{\rm b} = \frac{1}{2} \int_{-r_s}^{r_s} dx n \Phi(x) = \frac{A}{2r_s} \left(1 - \frac{\exp(-\kappa r_s)}{\kappa r_s} \sinh \kappa r_s \right).$$
(2.33)

Therefore, the potential energy of this unit cell with one electron is

$$-\Phi(0) + V_{nn} = -\frac{A}{2r_s} + \frac{A}{r_s} \exp(-\kappa r_s) - \frac{A}{2\kappa r_s^2} \exp(-\kappa r_s) \sinh \kappa r_s$$
(2.34)

which is also the total energy per electron. Since the uniform density must be n = N/L, we have that the total energy is the integral of Eq. (2.34). In the low density limit, $r_s \rightarrow \infty$. So, the most important term in the Hartree energy, U, is the lead term $-(2r_s)^{-2} = -n^2$.

In the strictly correlated electron limit [84, 85], the coupling constant of the adiabatic connection connecting the KS system at the real system is taken to be sufficiently large to localize the electron's wave functions so that they appear as point-like and are well modeled by the Dirac delta function [29]. This limit applies well to the Wigner crystal phase and implies that the important pieces of the energy are the Hartree and exchange-correlation which relate as $U = -E_{\rm xC}$. The Hartree energy per length for our exponential interaction is n^2 . Expanding the exchange energy about small *n* reveals that the exchange energy per length's behavior is $-n^2/2$. This requires the correlation energy to be $-n^2/2$ to counter balance the Hartree energy and avoid a self interaction error.

So far, our analysis has focused on the unpolarized case. The polarized case has a different behavior in the low density limit as can be seen by spin scaling the exchange energy. This will determine how we construct the local spin density approximation (LSDA), the generalization of LDA for polarized and partially polarized systems. The polarized exchange energy relates to the unpolarized exchange energy as $E_x^{\text{pol}}[n^{\text{pol}}] = E_x^{\text{unpol}}[2n^{\text{unpol}}]/2$ [Burke and friends]. This gives the revised low density limit for the polarized gas as $-n^2$ which completely cancels the Hartree energy in this limit! This implies that correlation must be of some higher power than 2 as there is no correlation energy in this limit.

However, in the following we will find that a fit to a correlation energy depending like $-n^2/\eta$ will provide a suitable parameterization for our data for some undetermined coefficient η . We now proceed to deriving the high density behavior for the correlation energy.

2.8.3 High Density Limit

With the low density limit well characterized, we turn to the high density limit. The random phase approximation (RPA) must be evaluated to determine the relationship [73, 74]. In this limit, one decomposes the real, many-body Hamiltonian for a number of particles to expand around the electron-electron interaction. The sum at each order of peturbation theory relies on assuming the dominant part of the energy is well characterized by the first diagram (also known as the "ring diagram") in the self-energy [78].

Despite some early misconceptions in the literature, RPA does not decrease its usefulness in low dimensional systems [75, 76, 77]. In fact, by capturing the plasmon frequency exactly, regardless of the form of the interaction, RPA is describing the long wave-length limit which precisely

corresponds with the high density/long wavelength limit.

Rewriting the electron-electron operator in the real, many-body Hamiltonian, the second quantized form [78], we may examine the correlation function in the two particle Green's function formalism. The term V_q is the Fourier transform of the electron-electron interaction,

$$V_q = \int_{-\infty}^{\infty} dx A \exp(-\kappa |x - x'|) \exp(iqx) = \frac{2A\kappa}{\kappa^2 + q^2}.$$
(2.35)

We note that this form is identical to the Fourier transform of the soft-Coulomb interaction if $A = \kappa = 1$.

The vacuum polarization diagram has a well known form in 1d [78, 79, 80],

$$\Pi_{0} = \frac{1}{q\pi} \ln \left[\frac{\omega^{2} - \left(\frac{q^{2}}{2} - \frac{\pi}{4r_{s}}q\right)^{2}}{\omega^{2} - \left(\frac{q^{2}}{2} + \frac{\pi}{4r_{s}}q\right)^{2}} \right].$$
(2.36)

This is taken as the entire contribution to the self-energy. The system's correlation energy is given by [78, 81]

$$E_c = \int \frac{dqd\omega}{(2\pi)^2} \operatorname{Im}[\ln\left(1 - V_q \Pi_0\right) + V_q \Pi_0]. \qquad (2.37)$$

The integration over q is best split into three regions, $\int_{-\infty}^{\infty} = \int_{-\infty}^{\kappa r_s} + \int_{-\kappa r_s}^{\infty} + \int_{\kappa r_s}^{\infty}$. In the limit where RPA is valid (*i.e.*, that of $r_s \to 0$), the middle integral goes to zero by the midpoint rule since for small intervals of integration the integral is well approximated by $\int_{-\kappa r_s}^{\kappa r_s} F(x) dx = 2r_s F(r_s)$. The first and third regions of integration are identical.

Examining the term $V_q\Pi_0$, we see that substituting $q \rightarrow q/r_s$ provides the opportunity to expand this term about small r_s . Using the specific form of V_q for this interaction, we notice that an expansion as a geometric series is available so long as we consider $q > r_s$ hence motivating the consideration

of three intervals of integration. The logarithmic quantity may be expanded about the argument, written in a variable z, to first order if r_s is the limit of being infinitesimal, $\ln[(1+z)/(1-z)] \approx 2z = 2\pi q^3/(4r_s^4\omega^2 - q^4 - \pi^2 q^2/4)$, since q^3 is always valued between $q^4 + q^2$ or equal to (in the special case where q = 1) leading to $q^3/(q^4 + q^2) \le 1$ always. The correlation energy at this point takes the form

$$E_{c} = \frac{2}{r_{s}} \int_{0}^{\infty} \int_{\kappa r_{s}}^{\infty} \frac{dq d\omega}{(2\pi)^{2}} \operatorname{Im} \left\{ \ln \left[1 - \kappa A \frac{4}{1 + \frac{\kappa^{2} r_{s}^{2}}{q^{2}}} \frac{r_{s}^{3}}{4 r_{s}^{4} \omega^{2} - q^{4} - \frac{\pi^{2}}{4} q^{2}} \right] + \kappa A \frac{4}{1 + \frac{\kappa^{2} r_{s}^{2}}{q^{2}}} \frac{r_{s}^{3}}{4 r_{s}^{4} \omega^{2} - q^{4} - \frac{\pi^{2}}{4} q^{2}} \right\}$$
(2.38)

With a substitution of $\omega \to \omega/r_s^2$, rewriting the term $(1 + \frac{\kappa^2 r_s^2}{q^2})^{-1}$ in a geometric series, and expanding the remaining logarithm, we see that the surviving low order terms (those remaining after subtraction) are

$$E_{c} = -\frac{1}{r_{s}^{3}} \int_{-\infty}^{\infty} \int_{\kappa r_{s}}^{\infty} \frac{dqd\omega}{(2\pi)^{2}} \operatorname{Im}\left\{ \left[4\kappa A \frac{r_{s}^{3}}{4\omega^{2} - q^{4} - \frac{\pi^{2}}{4}q^{2}} \right]^{2} \right\}$$
(2.39)

Using contour integration to evaluate the ω integral and choosing a half-circle contour closed in the upper half plane, we can evaluate the final integral to give

$$E_c^{\text{RPA}} = \begin{cases} -\frac{A^2}{\pi^4 n} & \text{unpolarized} \\ -\frac{A^2}{4\pi^4 n} & \text{polarized} \end{cases}$$
(2.40)

The above calculations are summarized for the unpolarized case. The polarized case relies on changing the spin sum in the vacuum polarization (so that $\Pi_0 \rightarrow \Pi_0/2$).

To check the rather surprising result that the length scale, κ , of the exponential does not affect the RPA limits, we note that a simplified condition for the coefficient of the high density limit was derived by Rajagopol and Kimball in Ref. [82] using finite temperature methods and has been investigated in other works [9, 10, 11, 33]. This condition, that $\mu^{-1} = \int dq q V_q^2$, gives exactly the same limit as above.

With these two limits in the high and low density regimes, the uniform gas densities are determined and parameterized to Padé approximation which limits to these derived asymptotes.

Chapter 3

Machine Learning the Exact Density Functional

3.1 Overview

Having constructed a test system in the previous chapter, we use machine learning methods to directly access the exact functional and perform self-consistent computation.

We use the density-matrix renormalization group, applied to a one-dimensional model of continuum Hamiltonians, to accurately solve chains of hydrogen atoms of various separations and numbers of atoms. We train and test a machine-learned approximation to F[n], the universal part of the electronic density functional, to within quantum chemical accuracy. We also develop a data-driven, atom-centered basis set for densities which greatly reduces the computational cost and accurately represents the physical information in the machine learning calculation. Our calculation (a) bypasses the standard Kohn-Sham approach, avoiding the need to find orbitals, (b) includes the strong correlation of highly-stretched bonds without any specific difficulty (unlike all standard DFT approximations) and (c) is so accurate that it can be used to find the energy in the thermodynamic limit to quantum chemical accuracy.

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3.2 Introduction

Although widely used in solid-state physics, chemistry, and materials science [98], Kohn-Sham density functional theory (KS-DFT) with standard approximations fails for strong correlation [38, 39]. The prototype is the H_2 molecule. When stretched, the electrons localize on each site while remaining in a singlet state, but this is not captured by such calculations [97]. These kinds of difficulties have led to the popularity of many beyond-DFT schemes, ranging from the simple addition [99] of a Hubbard U to the use of dynamical mean field theory [100] as well as many others.

But even KS-DFT is too slow for many large calculations, such as those using classical MD or continuum mechanics [101]. The original DFT, first suggested in the Thomas-Fermi approximation [66, 102] and later justified by the Hohenberg-Kohn theorem [1], uses only pure functionals of the total density, $n(\mathbf{r})$. This "orbital-free" version has the potential to be much faster than even the most efficient KS implementations, because the KS equations need not be solved [103]. Several recent attempts have constructed machine-learning (ML) kinetic energy functionals specifically to bypass this step [104, 105, 106, 107]. These are designed to be used in conjunction with standard KS approximations to speed up such calculations, but not to improve their accuracy.

Meanwhile, beyond the world of DFT, density matrix renormalization group (DMRG) has become a standard tool for finding extremely accurate solutions to strongly correlated lattice problems [108, 109, 110, 111]. In recent years, a one-dimensional analog of ab-initio Hamiltonians has been developed, using typically about 20 grid points per atom and interactions involving many grid



Figure 3.1: Electronic energy of the infinite chain from a model learned from extrapolated chain densities and energies. The accurate value was calculated with infinite DMRG (see text). points, with the express purpose of rapidly exploring both conceptual and practical issues in DFT [4, 35, 36, 37, 38]. A particular advantage is that, since 2000 grid points is routinely accessible, this includes up to 100 atoms, and extrapolations to the thermodynamic limit are much easier than in three dimensions. Applications include a demonstration of the behavior of the KS gap in a Mott-Hubbard insulator [36] and a proof of convergence of the KS equations with the exact functional, regardless of the starting point or strength of correlation [35].

In the present work, we combine all these methodologies to demonstrate several important features. We perform DMRG calculations on a variety of one-dimensional hydrogen atom chains, with from 2 to 20 atoms, and whose interatomic spacing R varies from 1 to 10 Bohr radii, and use these to train a ML model of F[n], the "universal" part of the density functional identified by Hohenberg-Kohn. This simulanteously includes both the non-interacting kinetic energy sought in orbital-free DFT and the exchange-correlation energy that is approximated in KS calculations. We demonstrate that, with reasonable amounts of training, we can *self-consistently* calculate densities and energies for these chains at new values of R, outside the training set, with quantum chemical accuracy. This includes highly stretched systems which are strongly correlated, and where all popular DFT approximations fail. We furthermore extrapolate the DMRG densities from the center of finite chains to the infinite chain limit, i.e., a one-dimensional (1D) solid. We train a new ML model and find we can solve self-consistently the solid problem at the same level of accuracy. Fig. 3.1 shows the convergence of our ML method for a typical separation of the infinite chain with respect to the number of training points. The horizontal lines show two independent DMRG estimates of the energy.

3.3 Background

3.3.1 DFT

The Hohenberg-Kohn theorem [1] establishes that the ground-state energy and density of a manybody problem may be found by minimizing a density functional:

$$E = \min_{n} \left\{ F[n] + \int d^3 r n(\mathbf{r}) v(\mathbf{r}) \right\},$$
(3.1)

where $n(\mathbf{r})$ is the single-particle density, normalized to *N* particles, and $v(\mathbf{r})$ is the one-body potential. The functional *F* can be defined via a constrained search as [112]

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$$
(3.2)

where \hat{T} is the kinetic energy operator and V_{ee} is the electron-electron repulsion operator, while Ψ is a normalized antisymmetric (for fermions) wavefunction. While this showed that the old Thomas-Fermi theory [66, 68, 102] was an approximation to an exact formulation, few modern calculations perform such a direct minimization. In practice, almost all calculations use the famous Kohn-Sham (KS) scheme, which uses an auxillary set of non-interacting orbitals in a single, multiplicative potential whose density is defined to match that of the original system, and in terms of which we can write

$$F[n] = T_{\rm s}[n] + U[n] + E_{\rm XC}[n], \qquad (3.3)$$

where T_s is the non-interacting kinetic energy of the KS electrons, U is the Hartree self-repulsion, and E_{xc} is the exchange-correlation energy (defined by this equation).

The genius of the KS formulation is that $E_{\rm XC}$ is typically a small fraction of F, so that much higher accuracy can be achieved by approximating only this component. The cost of the KS scheme is formally N^3 , the cost of solving for the orbitals. Much of modern DFT research is devoted to improving approximations to $E_{\rm XC}$, within which all quantum-many body effects are contained (by definition). The smaller field of pure DFT, also known as 'orbital-free', aspires to approximate $T_{\rm S}[n]$ directly, as in the old TF theory [66, 102], and thus bypass the need to solve the KS equations.

Many modern XC approximations are local or semilocal, i.e., use the density and its gradient to approximate the XC energy density at a point. While remarkably useful results can be obtained with such approximations, there remains a classic failure that can be understood in terms of the simple H₂ molecule [94]. Those approximations work well in the vicinity of the equilibrium bond length, but as the bond is stretched, they fail more and more badly. In the limit of a large but finite bond length (which we call stretched), a spin-restricted calculation yields the highly inaccurate energy of two unpolarized H atoms. On the other hand, an unrestricted calculation yields an accurate stretched energy, but has broken spin symmetry. Neither situation is satisfactory [97], most modern semi-local approximations fail in this way [94, 113] and efforts to overcome such difficulties are ongoing [114, 115]. An analogous failure occurs for semilocal approximations to $T_{\rm s}[n]$ when bonds are stretched in orbital-free DFT. Fig. 3.2 illustrates the failure of semilocal XC,



Figure 3.2: Binding curve for a 1D H_2 molecule. Black: highly accurate, converged DMRG results. Blue: LDA result restricted to a spin singlet.

by comparing the blue restricted LDA curve with the black DMRG curve. There is a huge error in the stretched limit.

3.3.2 DMRG benchmark data

It is difficult to overemphasize the utility of benchmark quantum chemical calculations for the development of DFT. The DFT revolution in quantum chemistry was made possible by the existence of the well-tested G2 data set for small molecules, and databases in quantum chemistry have proliferated ever since. On the other hand, calculations of "quantum chemical" accuracy, i.e., errors below 1 kcal/mol, are much more difficult and rarer for solids. A recent heroic effort [116] was made for benzene, a molecular crystal.

For the present study, we need to consider chains of up to 20 H atoms, with many different values

of the interatomic spacing ranging from about 1 to 10 Bohr. Extracting this large amount of data at the required level of accuracy from a quantum chemical code would be extremely demanding, if not impossible, given the strong correlation effects when the bonds are stretched.

Recently, DMRG has been applied to a one-dimensional analog of real-space Coulomb-interacing Hamiltonians, for precisely the purpose of performing demanding, highly accurate benchmark calculations of strongly correlated systems. In particular, the interaction is modeled as

$$v_{\rm ee}(u) = A \exp(-\kappa |u|) \tag{3.4}$$

where A = 1.071 and $\kappa^{-1} = 2.385$ [4] and *u* is the separation. This choice best mimics the popular soft Coulomb interaction, while having a single exponential allows DMRG to run very fast [4]. The one-body potential is then taken as $v(x) = -Zv_{ee}(x)$, where *Z* is the "charge" on a nucleus. Here Z = 1 for each H atom in the chain. This 1D analog allows rapid testing of novel ideas in electronic structure, especially those involving the bulk limit. Figure 3.2 is in fact for 1D H₂ with these parameters, and illustrates that the failures of standard DFT approximations such as LDA mimic those of three-dimensional (3D) Coulomb systems. The DMRG curve plateau is at twice the ground-state energy of one of these 1D H atoms.

3.3.3 Machine learning of the KS kinetic energy functional

ML is a set of algorithms developed to find hidden insights in data. It is widely used especially when the pattern behind complicated data is difficult to deduce explicitly. Successful applications include computer vision [117], cybersecurity [118], ancient abstract strategy games [119], etc.

Recently, in chemistry and materials science, machine-learning has become a popular tool for analyzing properties of molecules and materials, and finding specific functions from large data sets [120, 121]. But it has also been applied to the problem of finding density functionals, constructed
by interpolation from accurate examples. To date, the focus has been on the KS kinetic energy, $T_{\rm S}[n]$, partially because of the ready availability of data (every cycle of every one of the 30,000 KS-DFT calculations each year [98] produces an accurate example of $T_{\rm S}[n]$) and because of the enormous potential for speeding up routine DFT calculations.

The ML algorithm we used for modeling $T_{s}[n]$ is kernel ridge regression (KRR). It is a nonlinear regression method with an L2 regularization [122]. The density functional is represented as

$$T_{\rm s}^{\rm ML}[n] = \sum_{i=1}^{N_{\rm T}} \alpha_i k[n, n_i], \qquad (3.5)$$

where $N_{\rm T}$ is the number of training data, $n_i(x)$ are the training data and $k[n, n_i]$ is a kernel, some measure of the "similarity" between densities. Throughout this work, we use a Gaussian kernel,

$$k[n,n'] = \exp(-\|n-n'\|^2/2\sigma^2), \qquad (3.6)$$

where

$$||n - n'|| = \int dx [(n(x) - n'(x)]^2.$$
(3.7)

Such a kernel is standard in KRR, and has yielded excellent results in previous studies of $T_s[n]$ [106]. The weights $\alpha = (\alpha_1, \dots, \alpha_{N_T})$ are found by optimizing the cost function

$$\mathscr{C}(\alpha) = \sum_{i=1}^{N_{\rm T}} (T_{\rm s}^{\rm ML}[n_i] - T_{\rm s}[n_i])^2 + \lambda \alpha^{\rm T} \mathbf{K} \alpha$$
(3.8)

where **K** is the kernel matrix, $K_{ij} = k[n_i, n_j]$. The regularization strength λ and length scale σ are hyperparameters which are found via cross validation. A crucial principle in kernel ridge regression is the separation of the training data from the test data. A test set is constructed entirely independently from the training set. The cross-validation to find the hyperparameters occurs using only training data. The resulting approximate functional is tested only on the test data.

While highly accurate results for $T_s[n]$ can be found with relatively little data [104], it was immediately realized that the corresponding functional derivative is highly *inaccurate*. This is unfortunate, as the practical usefulness of an accurate model for $T_s[n]$ is in finding the density via solution of the Euler equation (for the KS system):

$$\frac{\delta T_{\rm s}}{\delta n(x)} = -v_{\rm s}(x),\tag{3.9}$$

where $v_s(x)$ is the KS potential. This difficulty has been surmounted in a sequence of increasingly sophisticated methods [105, 106, 107], each of which constrains the density search to only the manifold of densities spanned by the data, avoiding searching in directions for which there is insufficient data to evaluate T_s accurately. With such techniques, it has been possible to demonstrate an ML T_s functional that correctly mimics the KS solution even as a bond stretches [105], something impossible for any local or semilocal approximation to T_s . The value of this is to cut down the computational cost of large, repetitive KS calculations, but one still uses some standard XC approximation. Thus a machine-learned functional for T_s can, at best, reproduce the incorrect LDA curve of Fig. 3.2.

3.4 Method

In all applications in this work, we generate a large data set of highly accurate results generated using DMRG. We use a real-space grid with spacing 0.04, which has previously been shown to be sufficient to converge the results [4]. We calculate the energies and densities of chains of even numbers of atoms, from 2 to 20, with interatomic separations between 1 and 10 Bohr. Higher accuracy is achieved when every atom is centered on a grid point, discretizing the set of allowed separations. The specific separations used are listed in the Appendix.

Then a subset of these data are left out as test set. The training set, with $N_{\rm T}$ values of R, are collected



Figure 3.3: Same as Fig. 3.2. The green curves are ML with $N_T = 5$ on both the exact (dashed) and ML-optimized (solid) densities. The red solid curve is the ML with $N_T=20$ (number of training points) on ML-optimized (solid) densities. Black dashed curve is the exact DMRG curve, matching nearly exactly the $N_T=20$ on ML line.

from the remaining data. These are chosen to be as close to equally spaced as practical. The test set is excluded from the data where the training set is sampled from, to avoid contamination via the cross-validation process.

3.4.1 Machine-learned F[n] for a given molecule

The first improvement on previous work is to apply ML to F[n] itself, not $T_s[n]$ as in earlier work [105]. All the equations of Sec. 3.3.3 apply directly, by replacing $T_s[n]$ with F[n] and $v_s(x)$ with v(x). It is not *a priori* obvious that one might not encounter some difficulty, as F[n] contains all the many-body physics of the ground state.

We continue to use the H₂ molecule to illustrate our method. Contrary to previous work, we apply



Figure 3.4: Optimal densities for 1D H₂ molecule in the test set: DMRG (black dashed), ML with N_T =5 (orange solid), ML with N_T =20 (red solid).

KRR algorithms to ML the interacting functional F[n] itself, by training on highly accurate DMRG energies and densities at various values of R. In Table 3.1, we list the errors for H₂ as a function of $N_{\rm T}$, both on the exact density and on an optimally constrained density found by the methods of Ref. [123].

To illustrate the procedure, in Fig. 3.3, we show the energies with only 5 training points, R = 1.00, 3.20, 5.48, 7.76, 10.00, yielding the smooth, green dashed curve, when evaluated on the exact densities. The curve (almost) exactly matches at the training points, but is noticeably inaccurate inbetween. But note that, in contrast to all previous studies, we are fitting the full F[n], not just $T_S[n]$, so that, e.g., our inaccurate curve dissociates H₂ correctly, while no standard DFT calculation, with a standard XC approximation, can.

The problem is actually much greater than even the smooth dashed green curve would suggest. In

practice, we not only need the energy functional, but also its derivative, at least in the vicinity of a solution density. This is because we use the functional to find the density itself, via the Euler equation

$$\frac{\delta F}{\delta n(x)} = -v(x). \tag{3.10}$$

In fact, the derivatives of ML functionals such as that of Eq (6) are highly inaccurate and cannot be used to find the minimizing density. Methods have been developed to constrain the search to the manifold of training data via non-linear gradient denoising (NLGD) [123]. For our H₂ with $N_{\rm T} = 5$, these lead to the (even worse) solid green curve of Fig. 3.3. The optimal density is shown in Fig. 3.4. We clearly see that (a) the accuracy is not high enough and (b) the error is dominated by the error in the densities. (This is called a density-driven error [124] in a DFT calculation.)

However, when we increase to 20 data points, the ML curve (red solid) is indistinguishable from the exact one, and the error at equilibrium is only 0.007 kcal/mol, and shrinks with increasing R. This calculation applies all the principles discussed in Ref. [105], but is now applying them to the many-body problem, not just the KS problem. Even in the stretched limit, where the system is strongly correlated, there is no loss of accuracy. Note that we are not just fitting the binding curve, as we are reproducing the many-body density at every value of R, starting from data at a limited number of values. In Fig. 3.4, we plot the optimally-constrained densities at R = 4.0 (outside all training sets) for $N_{\rm T} = 5$ and $N_{\rm T} = 20$, compared with the exact density.

Here, ML has entirely bypassed the difficulty of solving the many-fermion problem. The machine learns the characteristics of the solution without ever solving the differential equation. Moreover, the HK theorem is a statement of the minimal information needed to characterize the ground-state of the system. In some ways, this ML approach is the purest embodiment of the HK theorem.

We note that the Euler equation (3.10) is merely the same as in KS theory but with T_s replaced by *F*. Thus, the entire algorithm for learning is synonymous with the previous works [105] but with



Figure 3.5: Partition density of each H atom in H₈.

 $T_{\rm S}$ replaced by F[n].

3.4.2 Finding a data-driven optimal basis for longer chains

The cost of optimal gradient descent methods, evaluated on a spatial grid, grows very rapidly with the number of grid points, and rapidly becomes unfeasible as the number of H atoms grows. Thus a simpler representation of the density is required. To overcome those difficulties, we introduce a basis set. Inspired by the localized atomic bases used in most quantum chemical codes, we developed a data-driven basis set using Hirshfeld partitioning [125] and principal component analysis (PCA).

To partition a molecular density via the Hirshfeld scheme, begin with the protomolecule of overlapped atomic densities at the nuclear positions of the real molecule. If $n_i^0(x) = n_1^0(x - (i - 1)R)$ is an isolated atomic density at the *i*-th nuclear center, spaced *R* apart, then

$$n^{0}(x) = \sum_{i=1}^{N} n_{i}^{0}(x)$$
(3.11)



Figure 3.6: Single H atom densities for H atoms in different chains and atomic distance (gray). The average density is plotted in red.



Figure 3.7: First 7 principal components of the densities shown in Fig. 3.6, from top to bottom.

is the density of the protomolecule, where R is the interatomic spacing. We define a weight

$$w_i(x) = n_i^0(x)/n^0(x),$$
 (3.12)

associated with each atom, and then define the density of each Hirshfeld atom within the real molecule as

$$n_i(x) = w_i(x)n(x), \tag{3.13}$$

where n(x) is the exact molecular density. The ground state density of a single hydrogen atom $n_i^0(x)$ is reported in Ref. [4]. Fig. 3.5 shows partition densities $n_i(x)$ of atoms in one H₈.

Next, for a specific chain length *N*, we consider a range of interatomic separations *R*, and consider the collection of every atomic density within the chain for every value of *R* in a training set, each centered on the origin, as shown in Fig. 3.6. These individual atomic partition densities reflect the diverse behaviors caused by the interaction between the hydrogen atoms inside the chains. A principal component analysis is applied to these densities, and the eigenvalues are ordered in decreasing magnitude to find a subspace with the maximum variance. Each atomic density can be accurately represented by the base density $f_0(x)$ (red in Fig. 3.6) and 7 principal components (Fig. 3.7),

$$n_i(R,x) = f_0(x) + \sum_{p=1}^7 c_{i,p}(R) f_p(x)$$
(3.14)

where *i* is the index of atom and *p* is the index of principal components. Thus the total density of H_N with separations *R* is $\sum_{i}^{N} n_i(R, x)$, and is described by just 7*N* coefficients. Note that $f_0(x)$ is very close to an isolated atom density, but we use the average to center our data for the PCA analysis. Our representation greatly reduces the number of variables in the density representation for a given chain length, and saves a significant amount of computational cost when solving for the ground state density of the system. This new basis set is completely data-driven and physically



Figure 3.8: Learning curves for several 1D H chains. (a) ML using the total density. (b) ML using the bulk partition densities (see text).

meaningful. Further, the derivation of this method is not limited to 1D.

We next repeated these calculations for a sequence of chains of increasing length. In each case, we train $F^{\text{ML}}[n]$ on a limited training set, and then compare on a test set (see Appendix), with the accurate results supplied by DMRG. The learning curves, i.e., error as a function of N_{T} , of chains of differing length, are shown in Fig. 3.8(a). The error typically decreases with amount of training data, but for fixed N_{T} , longer chains display substantially larger errors. This is because the binding energy curve changes more rapidly when the chain length is increased.

In applied machine learning, feature engineering, which uses domain knowledge of the data to improve the efficiency of ML algorithms, is a crucial step. Here, we know that as the chain length increases, the central density should converge to a fixed value (thermodynamic limit). We therefore choose the central two atomic densities alone to use as a minimal input feature for learning the energy of a given finite chain. The learning curves for models trained only on this central partition

Ν	NT	λ	σ	$\overline{ \Delta E_{\rm F} }/N$	$\max \Delta E_{\rm F} /N$	$\overline{ \Delta E }/N$	$\max \Delta E /N$	$E_{R=9.8}^{\mathrm{ML}}/N$	$E_{R=9.8}^{\mathrm{DMRG}}/N$
2	5	$1.0 imes 10^{-8}$	1000	2.54	7.02	9.74	20.3	-421.291	-425.797
2	20	$4.6 imes 10^{-10}$	2.15	0.00121	0.00802	0.005	0.013	-425.785	-425.797
2	50	$1.0 imes 10^{-12}$	0.70	0.00003	0.00034	0.050	0.304	-425.798	-425.797
4	50	$2.2 imes 10^{-11}$	46.4	0.0021	0.016	0.005	0.017	-428.617	-428.620
8	50	$1.0 imes 10^{-4}$	2.15	0.011	0.31	0.28	1.68	-430.011	-430.032
12	50	$1.0 imes 10^{-12}$	0.46	0.0031	0.010	0.24	0.88	-430.502	-430.503
16	50	$2.2 imes 10^{-11}$	0.46	0.0042	0.012	0.08	0.41	-430.738	-430.738
20	50	$2.2 imes 10^{-11}$	0.46	0.0042	0.014	0.26	0.88	-430.880	-430.880
∞	50	$1.0 imes 10^{-8}$	0.46	0.012	0.050	0.073	0.27	-431.447	-431.444

Table 3.1: ML performance on different chains H_N . N_T is the size of training set. Regularization strength λ and kernel length scale σ are the model hyperparameters selected by cross validation. The functional driven error ΔE_F is tested on the entire test set to show the overall accuracy. The total error $\Delta E/N$ is tested on the equilibrium test set to emphasize accuracy around equilibrium position. $E_{R=9.8/N}$ shows that ML can get very accurate dissociation limit. All errors are given in kcal/mol.

density are shown in Fig. 3.8(b). For chain lengths greater than or equal to 12, substantially greater accuracy is reached for a fixed amount of training data. Here we still use the total density for $N \le 8$ and the bulk density for $N \ge 12$. The model performance and hyperparameters are presented in Table 3.1.

3.4.3 Extrapolation to the thermodynamic limit

Our ultimate goal is to use ML to find the energy of the infinite chain to within chemical accuracy, for all interatomic separations. To do this, we first build a set of infinite chain energies and densities. For each value of R, we extrapolate both the density and energy of our finite chains as a function of N. This then gives us a set of data for the infinite chain that we can both train and test on and gave rise to Fig. 3.1. Figure 3.9 shows the extrapolation DMRG electronic energy curve. The ML results match nicely.

In an entirely separate calculation, we also performed DMRG directly for the infinite chain, using



Figure 3.9: Electronic energy per atom in the thermodynamic limit, both via DMRG chains (extrapolated to infinity) and using machine learning with 50 data points per chain.

the method of McCulloch [126] for a four atom unit cell.¹ The system is initialized by solving the equivalent finite size system with box edges at R/2. As a part of the iDMRG algorithm [126], a single unit cell is then inserted into the center of the finite system and 15 sweeps are performed over the inserted unit cell. The sequence is repeated–after adding another unit cell–until convergence. We compare these energies with the extrapolated values, finding agreement to within 1 kcal/mol for all values of R. This agreement validates our extrapolation procedure. We find that, with 50 data points, the ML result, on the optimized density, also agrees to within 1 kcal/mol. Thus, armed with the 50-data-point machine learned functional, one can self-consistently find the density and energy of the infinite chain to quantum chemical accuracy.

Our final figure, Fig. 3.10, simply demonstrates that the error for the infinite chain (and for all the ML calculations) is almost entirely due to the error in the optimized density. The functional-driven

¹Calculations were performed using the ITensor Library: http://itensor.org/



Figure 3.10: For a given training set with N_T training points, the functional driven error, ΔF_F per atom is shown in red (lower curve). The upper curve is the total energy error per atom evaluated self-consistently.

error [124] is the energy error made on the exact density:

$$\Delta E_F = E^{\rm ML}[n] - E[n] = F^{\rm ML}[n] - F[n].$$
(3.15)

We see that, at any level of training, ΔE_F is an order of magnitude smaller than the final energy error on the optimized density. Thus the error is density-driven but, nonetheless, can be forced down to quantum chemical limits with enough data.

3.5 Discussion

We have shown that it is in principle possible to construct, via machine learning, the entire interacting functional of Hohenberg and Kohn, F[n], so accurately that optimized densities and energies evaluated on them are within quantum chemical accuracy. We have done this using the 1D simulation of continuum Hamiltonians established over the last several years, and using DMRG as an efficient solver. We apply the ML methods previously developed for approximating the noninteracting kinetic energy. Here, because we have precise energies for the interacting system to train on, we are able to construct the interacting functional, including all exchange and correlation effects. Our ML functional has no difficulties when bonds are stretched so that correlations become strong. We have even managed to apply this methodology to chains extrapolated to the thermodynamic limit, producing chemically accurate results for solids. This level of accuracy is far beyond that of any existing DFT calculation of a solid.

We conclude with a discussion of the steps needed to generalize this calculation to realistic solids. The first point is that, while we have performed the present calculations in 1D for both computational and programming efficiency, there is absolutely no reason they could not be repeated for real 3D hydrogen chains. These can readily be treated using DMRG [127, 128] and the ML algorithms are independent of the dimensionality. The extrapolation to an infinite chain limit should behave in a similar fashion. While the algorithm for generating a model of F[n] was already developed, merely replacing T_s in the algorithm in Refs. [105, 106] with F[n], this is the first demonstration that this algorithm works for interacting electrons. The ground-state density is solved by the techniques of Ref. [123]. However, instead of using a spatial grid, a data-driven atom-centered basis set for the density is developed. The distance metric, derivatives, and second derivatives are calculated on these basis functions. This greatly reduces the number of variables in the algorithm. For H₂₀, the calculation in this new basis can easily be performed on a personal laptop.

We note also that the (relatively) large amount of data needed to achieve chemical accuracy is

solely because we have chosen to approximate the entire HK functional F[n] and also need to find its derivative sufficiently accurately to produce an accurate energy. If, instead, we had used the KS scheme with a standard approximation for $E_{\rm XC}$, we could used ML simply for the error in that approximation, yielding inherently much more accurate densities, and requiring much less data for the same level of accuracy in the energy.

More generally, an accurate general purpose solver such as QMC or accurate quantum chemical methods could be used to provide the highly-accurate data needed to train the machine learning. For 2D or 3D solids, extrapolation to the limit requires many more atoms. But since e.g., a 20x20x20 array is emminently practicable within KS-DFT, this is accessible with a machinelearned correction. Thus, at least within KS-DFT, there is no reason that an ML-constructed functional could not be created from QMC data to extract the bulk energy of a solid.

It has also recently been shown [129] that the amount of data needed to bypass the KS equations can be greatly reduced by learning the density as a functional of the KS potential, so that the functional derivative of the KS kinetic energy is never used. This was demonstrated for 3D molecules.

Lastly, we mention that the geometries used here are rather simple. We have not attempted to create ML-functionals that apply to many different atoms in many diverse bonding situations, as has been done in other work, and our functionals do not apply outside the domain they have been trained on. But since the energy curve of a bulk solid does not require such a functional, our ML approximation is sufficient for the purpose here.

Ultimately, any ML method can be limited by the need for excessive training. But our work here shows that this is possible in principle, and there is no reason to think it more difficult in practice.

3.6 Supplementary Material for Machine Learning the Exact Density Functional

3.6.1 Description of Data

The density matrix renormalization group (DMRG) [108, 109, 110, 111] has become the gold standard for calculations in one dimension. The ansatz made for the wavefunction is that of a matrix product state (MPS). This ansatz allows for a site-by-site determination of the wavefunction by concentrating on a small number (in our implementation, two) lattice sites at a time. Once the wavefunction is updated on those two sites, the next two sites are treated. The entire system is swept back and forth until convergence which usually occurs very quickly in one dimension.

To evaluate the Hydrogen chains in this work, an extended Hubbard model [4, 35, 36],

$$\mathscr{H} = \sum_{j,\sigma} \frac{-1}{2a^2} \left(\hat{c}_{j,\sigma}^{\dagger} \hat{c}_{j+1,\sigma} + \text{h.c.} \right) - \tilde{\mu} n_{j\sigma} + \sum_{j} v^j n_j + \frac{1}{2} \sum_{ij} v_{\text{ee}}^{ij} n_i (n_j - \delta_{ij}), \qquad (3.16)$$

can be constructed to recover the continuum limit in the limit of many sites. The prefactor on the kinetic energy terms is chosen to match the finite difference approximation for the kinetic energy with grid spacing *a*. An external potential is applied in the variable v^j while $\tilde{\mu} = \mu - \frac{1}{a^2}$ for chemical potential μ . Also, an electron-electron term, v_{ee}^{ij} is represented by an exponential function [4], This exponential mimicks the soft-Coulomb interaction, which itself is an approximation of the Coulomb interaction in 3d but spherically averaged [4]. The similarity between these functions gives the similar behaviors of the 1d atoms and their 3d counterparts when the symmetry is high.

Systems are calculated with open boundary conditions ("box" boundary conditions). The limit where the box boundary is far from the nearest atomic center is always taken, so no finite size

Ν	training set range	entire test set range	equilibrium test set range
2	$1.0 \le R \le 10 (146)$	$1.2 \le R \le 9.8$ (80)	$1.2 \le R \le 3.12$ (19)
4	$1.4 \le R \le 10 (136)$	$1.6 \le R \le 9.8$ (80)	$1.6 \le R \le 4.08$ (25)
8	$1.4 \le R \le 10 (136)$	$1.6 \le R \le 9.8$ (80)	$1.6 \le R \le 4.28$ (27)
12	$1.6 \le R \le 10$ (131)	$1.8 \le R \le 9.8$ (80)	$1.8 \le R \le 4.32$ (26)
16	$1.6 \le R \le 10$ (131)	$1.8 \le R \le 9.8$ (80)	$1.8 \le R \le 4.32$ (26)
20	$1.6 \le R \le 10(131)$	$1.8 \le R \le 9.8$ (80)	$1.8 \le R \le 4.4$ (27)

Table 3.2: Hydrogen chain data. N is the number of Hydrogen atoms in the chain. R is the atomic distance between atoms. The number of DMRG data in each range is in parenthese.

effects appear.

A complication is apparent in 1d that does not appear in 3d. There is no angular momentum in 1d. Thus, not all neutral atoms bind their electrons. One can see this in a reduced example as follows: Consider a delta function interaction in 1d of the form $-\delta(x - R/2) - \delta(x + R/2)$ [29]. When R = 0, there is only one solution. At any finite *R*, the number of electrons that will bind increases from two. The same effect occurs for the exponential interaction, though it is not as easy to see.

This implies that a lower cutoff in the exponentially interaction hydrogen chains will impose a lower limit on suitable chain length. We are interested in systems that do bind all electrons, so a systems below a critical R are ignored. Table 3.2 lists the range of interatomic distances used for each chain. For each Hydrogen chain data generated by DMRG, first sample 80 data from the *entire test set range* in Table 3.2 equi-distantly. This test set is inaccessible in the training process. The rest of data in *training set range* in in Table 3.2 are used as grand training set, where the N_T training data are uniformly sampled to train the model. The *equilibrium test set range* is a subset of entire test set range, emphasizing the performance around equilibrium positions. The upper bound is around twice the equilibrium position given by DMRG result.

Chapter 4

Approximate natural orbitals from density functional theory

4.1 Overview

We return to the basis set used in Chapter 3 where a partitioning scheme was used to represent the density in only a few basis functions. This concept can be generalized for a given system into a basis set. But the particulars of the basis set from Chapter 3 were derived for a particular system and only had a few orbitals in it. We explore extending this concept to a more general class of functions here.

The concept of reproducing the natural orbitals of a given system is generalized to a series of local functions known as wavelets. The wavelet functions are embedded in a natural orbital mimic we call the product plane wave ansatz. This is a rapidly convergent set of functions that is based on the orbitals of an approximate single Slater determinant calculation such as Hartree-Fock or the local density approximation.

This is a paper that was submitted with Kieron Burke and Steven R. White.

In this chapter, we propose a general method for constructing system-dependent basis functions for correlated quantum chemical calculations. Our construction combines features from several traditional approaches: plane waves, localized basis functions, and wavelets. In a one-dimensional mimic of Coulomb systems, it requires only 2-3 basis functions per electron to achieve chemical accuracy, and reproduces the natural orbitals. We illustrate its effectiveness for molecular energy curves and chains of many atoms. We discuss the promise and challenges for realistic quantum chemical calculations.

4.2 Introduction

Many tens of thousands of electronic structure calculations are performed each year, the vast majority in a single-particle basis set of some sort. These calculations can be divided into two types: those that extract the energy from a set of single-particle occupied orbitals (denoted single-determinant) such as density functional theory (DFT) [1, 39, 40, 41, 130] or Hartree Fock (HF), and those that go beyond a single determinant, such as configuration interaction [131, 132], coupled cluster methods [133, 134, 135], density matrix renormalization group (DMRG) [42, 110, 111, 127, 136, 137], and some types of quantum Monte Carlo. Going beyond a single determinant is necessary for many systems, but is typically much more demanding computationally. Such calculations are more difficult because larger basis sets are needed to achieve chemical accuracy (1 kcal/mol), and computation times usually scale as a high power of the number of basis functions. These larger basis sets are needed to represent the electron-electron cusp in the wavefunction which exists at every point in space.

A natural question arises: what would be the optimal basis set for an electronic structure calculation, assuming the basis is specifically adapted to that system? For a single-determinant method, the answer is clear: the self-consistent occupied orbitals are the optimal basis for that calculation: used as a basis, they reproduce the exact energy and properties. The number of these basis functions (for a spin-restricted calculation) is thus $N_e/2$, where N_e is the number of electrons. Of course, this minimal basis does not offer a computational shortcut: the occupied orbitals must be determined in a separate, non-adapted basis calculation. Here, we are concerned with multi-determinant methods, and we will assume that the computation time for a traditional single-determinant calculation is small in comparison to the multi-determinant method.

For post-HF methods, there is *no* exact finite system-adapted basis: any finite basis introduces errors. However, the natural orbitals are close to the most rapidly converging single-particle basis, at least in terms of allowing the greatest possible overlap with the exact ground state [138, 139]. The natural orbitals are the eigenstates of the single-particle density matrix (also known as the equal-time one-particle Green's function). The number of nonzero eigenvalues (occupancies) is infinite. A (near) optimal basis of M_{no} orbitals consists of the M_{no} natural orbitals with the greatest occupancy.

One obvious weakness in using natural orbitals is that one does not know them until after one has solved the interacting system, using a post-HF method, with another larger basis. Iterative natural orbital methods are a way to reduce the computational expense, but *approximate* natural orbitals that did not need a post-HF method to determine them could be very useful [140]. But natural orbitals have another key weakness: they are (normally) completely delocalized across the system. This delocalization prevents a number of shortcuts that can greatly decrease computation times for large systems. Delocalization is especially harmful for low-entanglement methods such as DMRG, since there is no area law for the entanglement entropy in a delocalized basis.[141]

Here we describe an approach that starts with the occupied orbitals of a DFT (or HF) calculation, and yields basis sets which produce chemically accuracy in correlated calculations. We test this approach in 1D, using potentials that make 1D mimic 3D in many respects, and using DMRG [4]. The computational effort for the basis construction is minimal. The number of basis functions

needed is typically about $2M_{no}$, where M_{no} is the minimal number of natural orbitals needed to reach chemical accuracy, or about two or three times the number of electrons. We expect this method can be easily extended to quasi-1D systems (such as large-Z atoms or chains of real H atoms) and hope it can applied more generally in 3D.

The first step produces what we call "product plane waves" (PPWs) by multiplying the occupied orbitals by a set of low momentum cutoff plane waves. The lowest momentum is determined by the spatial extent of the entire system. This simple ansatz converges well in our tests in 1D, and we show how its convergence is within about a factor of 2 compared to natural orbitals. But a weakness of PPW's, shared with natural orbitals, is that the basis is not local. As the second major part of this work, we describe fragmentations of the PPW's that utilize wavelets [142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 154, 155, 156, 157, 158, 159, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186] to produce atom-centered adapted orthogonal bases with good completeness and locality. This approach requires only a modest additional number of basis functions to yield the same accuracy as PPW's, but with a smooth, local, and orthogonal basis.

4.3 Background

4.3.1 The one dimensional Hamiltonian

Our non-relativistic many-electron Hamiltonian, expressed in second quantized form, either in a basis set or on a grid, is [187, 188]

$$\hat{\mathscr{H}}^{\mathrm{MB}} = \sum_{i,j,\sigma} \left(t_{ij} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma} + \sum_{k,\ell,\sigma'} V_{ijk\ell} \hat{c}_{i\sigma}^{\dagger} \hat{c}_{j\sigma'}^{\dagger} \hat{c}_{\ell\sigma'} \hat{c}_{k\sigma} \right),$$
(4.1)

with fermionic operators \hat{c} labeled either by site or basis-function i, j, k, ℓ and with spin σ (or σ'). We define the 'exact' solution as solving this Hamiltonian on a very fine grid, which is close to the continuum limit[4, 35]. For both the grid and for basis functions, we find the exact many-particle ground state of these 1D reference systems using DMRG. The one-electron integrals are

$$t_{ij} = \int d\mathbf{r} \, \boldsymbol{\varphi}_i^*(\mathbf{r}) \left(-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) \right) \boldsymbol{\varphi}_j(\mathbf{r}), \tag{4.2}$$

where $\nabla^2 = \partial_x^2$ for the 1d calculations, $v_{\text{ext}}(\mathbf{r})$ is the external potential, discussed below. In a basis, with functions $\varphi_i(\mathbf{r})$, the two-electron integrals are

$$V_{ijk\ell} = \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \varphi_i^*(\mathbf{r}) \varphi_j^*(\mathbf{r}') v_{ee}(\mathbf{r} - \mathbf{r}') \varphi_k(\mathbf{r}') \varphi_\ell(\mathbf{r}).$$
(4.3)

On a grid, the interaction takes a much simpler diagonal form with $i = \ell$ and j = k, with the integral taking the value $v_{ee}(\mathbf{r}_i - \mathbf{r}_j)$. For grid calculations, we use the ITensor library, along with matrix product operator technology.[ITe] In the basis, we use the Block DMRG code since it is specifically tailored to avoid stationary states that are not the ground state in a basis set and has implemented the form of the Hamiltonian efficiently [137, 189, 190, 191, 192].

Previously, we have explored 1D potentials which mimic as closely as possible the behavior of real 3D systems. A particularly convenient choice matching a number of 3D features is a single exponential function, $v_{ee}(x-x') = A \exp(-\kappa |x-x'|)$ with A = 1.071 and $\kappa = 0.419$, and $v_{ext}(x) = -Zv_{ee}(x)$, where Z is the atomic number, just as in 3D. This particular function closely mimics the results from a soft-Coulomb interaction, but at a reduced cost for grid DMRG calculations[4, ITe]. This potential also more closely mimics 3D since it has a mild singularity at zero distance. In 3D, the Coulomb interaction is divergent, but its effect is moderated, and integrals over it are finite, because of the very small volume associated with the $r \rightarrow 0$ region, and the associated integration factor $4\pi r^2$. In 1D, we get qualitatively similar behavior from the slope discontinuity in the potential at r = 0. A local density approximation (LDA) was also derived for this interaction.



Figure 4.1: (color online) First two natural orbitals, labelled by their occupation numbers, of (1D) He. An X marks the location of the nucleus.

Our finite difference grid Hamiltonian looks like an extended Hubbard model[35],

$$\hat{\mathscr{H}}^{\text{fine}} = \sum_{i} \left(-\frac{1}{2\delta^2} \left(\hat{c}_{i+1}^{\dagger} \hat{c}_i - 2\hat{n}_i + \hat{c}_i^{\dagger} \hat{c}_{i+1} \right) \right) + \sum_{i} v_i \hat{n}_i + \sum_{i,j} \left(v_{\text{ee}}^{ij} \hat{n}_i (\hat{n}_j - \delta_{ij}) \right)$$

$$(4.4)$$

where the superscript "fine" indicates we will use this lattice on the finest (original) grid of spacing a = 1/32, $\hat{n}_i = \hat{c}_i^{\dagger} \hat{c}_i$, external potential v_i , and long-ranged electron-electron interaction v_{ee}^{ij} on sites *i* and *j*. A distance of 60 from the outermost grid points to the first or last atom is used for all systems that follow, allowing wavefunctions to have extended tails.

The natural orbitals are the eigenvectors of the one-particle reduced density matrix (RDM), which

is the equal-time one-particle Green's function, with matrix elements:

$$\rho_{ij} = \langle \hat{c}_i^{\dagger} \hat{c}_j \rangle. \tag{4.5}$$

The eigenvalues of ρ_{ij} are the occupation numbers and the eigenvectors are the natural orbitals, which we order in decreasing occupation. Fig. 4.1 shows the first two for 1D He, and we later show (Fig. 4.3) that, in a basis set of these 2 orbitals alone, the expectation value of the Hamiltonian is only 1 kcal/mol above the exact ground-state energy. The term chemical accuracy refers to errors not exceeding 1 kcal/mol, or 0.0015 Ha, and is often used as a standard for accuracy of quantum chemical methods for covalent bonds.

4.3.2 Wavelets

Wavelets were originally introduced by Haar in 1910 [142] but they have since been modernized and expanded by several works by Gabor [143], Grossman and Morlet [144], Meyer [145], Mallat [146], and Daubechies [147, 148, 149] and many others. These functions have become widely used in audio and image compression (such as jpeg and mp3 file formats). These were also connected to a quantum gate structure, tensor network algorithms, and compression of matrix product states [178, 179, 180].

Consider a localized function f(x) located near the origin. We can form a basis from this function by translating it by all integer translations, i.e., $\{f(x-j)\}$ for integer *j*. A wavelet transformation (WT) is a mapping of f(x) to an new function f'(x) defined by

$$f'(x) = \sum_{k} c_k f(xd - k),$$
 (4.6)

where *d* is the dilation factor, which is normally taken to be 2. The WT is defined by the coefficients c_k . We will only consider compact wavelets, for which the number of nonzero c_k 's is finite. The scaling function of the WT, S(x), is the fixed point of this mapping. The c_k are chosen cleverly to make the S(x - j) to be orthogonal for different *j*, and to have a number of other desireable properties, such as polynomial completeness up to a certain order[147]. The scaling function is designed to represent smooth, low momentum parts of functions. The scaling function is not a wavelet, although it does form the top layer of a wavelet basis. A wavelet is formed from S(x) using another set of coefficients w_k (which are defined in terms of the c_k):

$$W(x) = \sum_{k} w_k S(xd - k). \tag{4.7}$$

The wavelets capture higher momentum features.

A wavelet basis consists of scalings and translations of S(x) and W(x), and it is complete and orthonormal. It is characterized by a coarse grid with spacing Δ . At all integer multiples j of Δ , one puts a scaling function, of size Δ , namely $S(x/\Delta - j)/\sqrt{\Delta}$. Then, at scales Δ , $\Delta/2$, $\Delta/4$, etc., one puts down a grid of scaled wavelets, with the spacing and the size of the functions always equal. All these functions together are complete, and they are all orthogonal to each other. Some of the functions of a wavelet basis are shown in Fig. 4.2.

Wavelet bases are an attempt to have locality in both space and momentum simultaneously, as much as possible, subject to the constraint of orthgonality. The layer of scaling functions represent all momenta from 0 to roughly $O(1/\Delta)$; the coarsest layer of wavelets represents momenta from roughly $O(1/\Delta)$ to $O(2/\Delta)$, etc., but with significant overlap in the momentum coverage between different layers.

We have briefly described wavelet bases in terms of continuous functions, but they can equally be described in terms of WTs acting on an initial fine grid. The WTs we use are based on the fine grid



Figure 4.2: (color online) One of the scaling functions (solid blue line) and some of the wavelets (dashed lines) of a wavelet basis of type Coiflet-18. These functions are based on a fine grid with spacing 1/32, and the level parameter z gives the size-scale of each function as $2^{z}/32$. Both the scaling function and rightmost wavelet are at z = 5.

used by the grid DMRG calculations, and these are what is shown in Fig. 4.2.

Many different types of wavelet transforms have been constructed. Here we choose Coiflets, derived by Daubechies, which are characterized by the number v of nonzero c_k . We choose relatively high v to get good completeness and smoothness. Wavelets can be easily extended to higher dimensions by taking products such as S(x)S(y)S(z) [181], so the principal features of 1D carry over to 3D [176, 193, 194, 194, 195, 196, 197, 198, 199].

4.4 **Product Plane Waves**

In this section, we describe our new approach to design a specific system-dependent basis with as few functions as is practical. We first argue that the exact natural orbitals provide a natural least possible number, but rely on knowing the exact solution[138, 139]. We then show how to combine

planewave-type basis functions (PPW's), wavelet technology, and adaptation via approximate DFT (or other) single-particle orbitals, to create a basis with no more than about twice this number, but still yielding chemical accuracy. A crucial feature is that we never use more than a few of each kind of function, so that we never come close to being limited by the asymptotic convergence properties of any one set of basis functions.

4.4.1 Natural orbitals as a basis

We wish to find basis sets which, when solved exactly, gives ground-state energies at most about chemical accuracy (1 kcal/mol) above the exact, complete basis limit. We wish to find basis sets that converge to this accuracy with as few functions as possible, but also without needing to know the exact solution to determine them. With the fine grid DMRG wavefunction, we can calculate ρ_{ij} exactly and find the exact natural orbitals. Since our DMRG solutions do not break spin symmetry if the number of electrons is even, the up and down RDMs are identical. (For odd electron numbers, we average the up- and down-RDMS and use that to define our natural orbitals.)

The first two natural orbitals for a 1D helium atom were shown in Fig. 4.1. The natural orbitals yield the smallest number of basis functions that can be expected to yield chemical accuracy, i.e., when ordered by occupancy, the least number M_{no} which, when used as a basis, yields an error below chemical accuracy. Fig. 4.3 shows the energy error for a variety of systems, when the basis is chosen as a finite number of the most occupied exact natural orbitals. We see that $M_{no} = 2$ for He, but is 3 for H₂ either close to equilibrium (R = 2) or stretched (R = 4). For Li, $M_{no} = 4$, while Be has $M_{no} = 6$. Unstretched H₄ also has $M_{no} = 4$, but stretched H₄ requires $M_{no} = 7$. Thus M_{no} increases with the number of electrons, and also (slightly) with the number of centers.

Fig. 4.4 shows the first four natural orbitals for an H_4 chain, which is stretched. Clearly, the orbitals delocalize over the entire chain. We also see from Fig. 4.3 that even in this basis, there remains about 8 kcal/mol error, and 3 more orbitals are needed to reach chemical accuracy.



Figure 4.3: (color online) Energy errors for He, Li, Be, H₂, and H₄ when evaluated in a basis of N_f exact NOs of greatest occupancy.



Figure 4.4: (color online) Same as Fig. 4.1 but for H_4 at R = 4. X's mark the locations of the nuclei.

4.4.2 Constructing the basis

Given the orbitals from a HF or DFT calculation, perhaps the simplest conceivable basis would be the occupied HF or DFT orbitals, since this allows the reproduction of the single determinant. One well-known approach for enlarging this basis to allow for correlation is to use additional eigenstates of the Fock matrix, selected by an energy cutoff [162, 199, 199, 200]. It is clear, however, that this eventually becomes inappropriate. For a more complete basis, one needs functions with positive energy, but there are an infinite number of functions at zero energy far from the molecule. To remedy this, we could put a box around the molecule and include only functions within that box. However, this can be very wasteful, since the box needs to include extended tail regions, where additional basis functions are not very useful. Instead of using energies, we adopt a quite different approach, motivated by the construction of variational wavefunctions—in particular, Jastrow functions.

Single-particle determinantal states φ from DFT or HF are rough approximations to the manyparticle wavefunction, but can be improved substantially by multiplication by a Jastrow factor, \mathcal{J} , which provides explicit correlation. Modifying a determinantal wavefunction with a Jastrow factor is often the first step in designing a variational wavefunction for quantum Monte Carlo calculations [201] The Jastrow factor acts as a multiplicative factor for the wavefunction and simple form for \mathcal{J} is [202]

$$\mathscr{J}(\mathbf{r}_1, \mathbf{r}_2, \ldots) = \prod_{i < j} J_2(\mathbf{r}_i - \mathbf{r}_j).$$
(4.8)

The J_2 term is near 1 if \mathbf{r}_i and \mathbf{r}_j are far away, and becomes less than one as \mathbf{r}_i and \mathbf{r}_j come together, building in the electron-electron cusp. We now ask the question: what would be a good *single-particle basis* to represent \mathscr{J} or J_2 ?

The fact that J_2 is a function of the difference of two position vectors means that there is no benefit to increasing resolution in one region relative to another, at least for fitting J_2 . One does expect,



Figure 4.5: (color online) Product plane wave (PPW) functions for a 1d H₂ at R = 3. Here the box size is L = 7.72, and marked by pink vertical lines. The upper figure shows the windowing functions $\cos(k_1x)$ and $\sin(k_1x)$ and the lower figure shows the first three PPW's (the first is just the LDA orbital).

however, that longer wavelength functions are more important than short wavelength functions. This suggests that a plane wave basis, restricted to the general vicinity of the molecule, with a momentum cutoff which is not too high, is a reasonable approximate basis for a Jastrow function.

Since the Jastrow function in a variational wavefunction multiples the determinant of occupied DFT orbitals, this suggests a very simple ansatz for a basis for correlated calculations: the product of occupied orbitals and low momentum cutoff plane waves, which we call a product plane wave (PPW). To be more specific: let $\{b_k(\mathbf{r})\}$ be a set of plane waves with a low momentum cutoff, and let $\{\varphi_j(\mathbf{r})\}$ be the occupied orbitals from a DFT/HF calculation. Then our product plane-wave (PPW) basis is $\{\varphi_j(\mathbf{r})b_k(\mathbf{r})\}$. The momentum cutoff in $\{b_k(\mathbf{r})\}$ corresponds to some minimal resolution. Linear combinations of the $b_k(\mathbf{r})$ can represent a correlation hole at any position within the system, while high momentum behavior near the nuclei is captured by the $\{\varphi_j(\mathbf{r})\}$. $b_{k=0} = 1$, so that the $\{\varphi_j(\mathbf{r})\}$ themselves are part of the basis.

In generating a PPW basis, several choices must be made. First, we want to put the molecule in a "box" that defines the sequence of momenta in the plane waves. Since the detailed correlations we want from the plane waves are weak in the tails, and since the box size is only used to define momenta, we do not include long density tails. We simply choose a small density cutoff, ρ_m , to define the edge of our box, from our DFT (or HF) calculation. Here $\rho_m = 10^{-3}$ throughout, but we expect our qualitative results to be very insensitive to this choice. For neutral atoms, the corresponding box sizes are 4.90,5.34,8.40, and 8.71 for Z = 1 to 4. A simple example of a product plane wave basis is illustrated in Fig. 4.5. The first two functions resemble the natural orbitals of He in Fig. 4.1 and the natural orbitals here. This resemblence between PPW's and NOs tends to continue for higher functions, although the precise order of the functions can vary.

Let \mathscr{K} be the number of occupied orbitals in a DFT or other approximate calculation. Let L be the width of the box defined by the cutoff ρ_m . Then choose an integer $J \ge 0$ to create 2J + 1 trigonometric functions, $\cos(k_n x)$ and $\sin(k_n x)$, where $k_n = n\pi/L$, and multiply each by the occupied DFT orbitals, creating $(2J + 1)\mathscr{K}$ PPW's. These functions are exactly orthogonalized. The results for H₄ are shown in Fig. 4.6 and compared to the exact natural orbitals. The PPW's are remarkably close, especially for those orbitals that are occupied in the DFT calculation, but also even for those that are not.

Finally, in Fig. 4.7, we show the energies for our systems as a function of the number of PPW's. For He and H₂, $\mathcal{K} = 1$, so increasing J by 1 yields two more PPW's (the sine and the cosine); for the rest, $\mathcal{K} = 2$, and 4 PPW's are added each time. A quick glance shows a remarkable similarity to the ordered natural-orbital energy errors of Fig. 4.3. The PPW's functions yield chemical accuracy with few more functions than M_{no} , showing that they do not just look similar to the NO's, they are similar in an energetically meaningful sense. We denote M_{PPW} as the least number needed to reach chemical accuracy. A more careful inspection shows that they are not quite as accurate, even for He, and that the difference grows with the number of electrons and the number of atoms. It is most noticeable for stretched H₄, where $M_{PPW} = 18$, whereas $M_{no} = 7$. But this is still a remarkably



Figure 4.6: (color online) The first five PPW's (blue) compared to the exact natural orbitals (red dashed) for H₄ with R = 3. Here L = 13.8.



Figure 4.7: (color online) Finite-basis error of PPW's, to be contrasted with Fig. 4.3, which has exact NO's.

small number for a strongly correlated system.

4.5 Wavelet localization

So far, so good. Our PPW's yield chemical accuracy with about $2M_{no}$ basis functions. But, to be efficient, tensor network methods such as DMRG require the low entanglement that comes from localized basis sets. Other methods may also benefit from localized basis functions, which make Hamiltonians sparse. Now we study cases with more than one atom, showing how we can use wavelet technology to break down a PPW into localized, smooth orthogonalized basis functions, centered around each atom, without too large an increase in the number of functions.

Traditional methods for localization rely on orthogonal transformations within the set of basis functions one already has. Not enlarging the set of functions puts a strong limit on how localized the functions can be made. However, if one enlarges the space without limit, one can make the basis as local as one wishes. One can think of "chopping up" each delocalized basis function (which we can picture as a molecular orbital): partition all of space into a chosen number of disjoint regions, or *cells* [203, 204, 205, 205, 206]. For example, one can make the number of cells the same as the number of atoms, and define each cell by associating each point in space with the closest nucleus. Form a basis by projecting each delocalized basis function into each cell, i.e. multiplying it by a function which is unity for points in the cell and zero outside, and repeating for all delocalized functions. Linear combinations of chopped up functions would allow one to reproduce any of the original delocalized functions, but this would make a terrible basis, for two reasons: 1) discontinuous basis functions have infinite kinetic energy, and 2) the number of localized functions scales as the square of the number of atoms.

Using wavelets, we can retain this idea of "chopping up" basis functions into different regions, but fix these two problems. As discussed in 4.3.2, we define a complete wavelet basis consisting of a grid of scaling functions with lattice spacing Δ (say with $\Delta \sim 1$ Bohr), and an infinite sequence of wavelets at scales Δ , $\Delta/2$, $\Delta/4$, etc, as shown in Fig. 4.2. We will refer to any of these functions, either a scaling function or a wavelet of any scale, as a WF (wavelet-function).

Now to chop up a delocalized basis: expand all delocalized functions in terms of the WFs. Many WFs will not have significant overlap with any functions, and can be dropped. This procedure thus produces a localized but smooth basis encompassing the original functions, assuming one has chosen smooth wavelets. However, the number of functions tends to be rather high, so we use this only as a starting point.

Again we partition all of space into cells, associated with atoms. Associate each WF to a cell. A natural way to do this is to define a center of mass for each function, and then the WF goes in the cell that contains its center of mass. Now we can project each delocalized function into each cell, simply by expanding the function in terms of the WFs belonging to the cell. This cuts the delocalized function into pieces which are all orthogonal. An example of this procedure is shown in Fig. 4.8.



Figure 4.8: (color online) The function $\exp(-0.5 * |x+3|) + \exp(-|x-3|)$ (black dashed) is divided into two orthogonal pieces (red and green solid lines) using wavelets. The wavelet basis used was based on Coiflet-24 with $\Delta = 1$, and the dividing line separating the two cells (dotted line) was x = 0.9. The small oscillating tails make the two function pieces orthogonal. The two singularities each only appear in one piece, because the high momentum wavelets representing the singularities are more and more localized the higher the momentum.

If we repeat this with additional delocalized functions, the pieces in different cells will be orthogonal, even if they came from different delocalized functions, since the WFs of different cells are orthogonal. Within a single cell, the pieces will not be orthogonal, and may have substantial overlap. The final step is to recombine all the pieces in a particular cell into a reduced set of orthogonal functions for that cell, and repeat for all cells. Note that while the original delocalized functions may be normalized, the pieces come from a projection and will not be, and some pieces may have very small normalization. It is important to leave the pieces unnormalized. For each cell, we wish to find the minimal set of basis functions that can represent all the pieces to within a specified accuracy. This is a well known linear algebra problem with a simple solution. Let f_j^i be the piece of delocalized function *i*, expanded in terms of the WFs *j* belonging to a cell *c*. Form a cell covariance matrix ρ^c as

$$\rho_{jj'}^c \equiv \sum_i f_j^i f_{j'}^i \tag{4.9}$$

Then the reduced basis we seek is the set of eigenvectors of ρ^c (which is positive semi-definite) with eigenvalues above a specified cutoff, η . This cutoff is roughly the mean-square error in representing all the different pieces. This is often called a principal component analysis [207, 208, 209, 210, 211]. Here we call the entire process wavelet localization (WL) and the resulting basis functions wavelet-localized orbitals (WLO's). Although the WLO procedure could be applied to other delocalized bases, here we will only consider its application to PPWs.

Fig. 4.9 shows the results of wavelet localization for 1D H₄, with a spacing R = 2, discussed more in Sec. 4.5.1. For simplicity, the figure shows only the two leading eigenfunctions and their eigenvalues for only cells 1 and 3. The dashed lines show the dividing lines between the different boxes; the nuclei are at x = -3, -1, 1, and 3. The functions are all orthogonal, with oscillations in the tails of each function to ensure orthogonality between boxes.



Figure 4.9: Some of the WLO's for each cell of an H₄ chain. Shown are the first two in both the first atom's cell (far left) and third atom's cell. Green vertical lines are drawn midway between each atom and weights of each function are labeled near each curve. The calculation this was taken from was b = 0, $\Delta = 1.0$, $N_J = 0$.

The parameter Δ , the spacing of the scaling functions, is crucial, as it sets the size of the region in which functions on adjacent boxes overlap. In the limit $\Delta \rightarrow 0$, this chopping up procedure reduces to the naive discontinuous procedure mentioned at the beginning of this section. The procedure also becomes poorly behaved if Δ is larger than the interatomic spacing. Roughly, one should set Δ to a modest fraction of the interatomic spacing, but later on we show results as a function of Δ to determine optimal values.

Lastly, we note that, for multi-center stretched systems, if $R > L_a$, the box for an atom, then we use L_a instead of L for that cell. This can greatly increase the number of functions to $N_a \times N_{fa}$, where N_{fa} is the number needed to reach chemical accuracy for the isolated atom, but unneeded functions will be discarded by our wavelet localization.


Figure 4.10: Error as a function of bond length R for H₂ using both pure PPW's and WLO's, for various values of J. The sudden shift is at the Coulson-Fischer point of the LDA calculation, beyond which a broken spin-symmetry solution, with twice as many orbitals, has the lowest energy.

4.5.1 Performance of WLO bases

In this section, we wish to check that our WLO's work well for typical quantum chemical calculations, and find out how many WLO's are needed for a given task. Our procedure requires, at most, $N_{occ} \times (2J+1) \times N_{cell}$ functions. Thus, for a H₄ chain that is unstretched (no spin-symmetry breaking), $N_{occ} = 2$, we will usually choose J = 1, and have 4 cells. A PPW calculation has 6 functions, and up to 24 (6 per cell) when fragmented. However, in practice, up to half those functions can be eliminated by the cutoff of our covariance matrix. This removal of irrelevant functions becomes increasingly important as the number of atoms grows.

The prototype calculation is the dissociation of molecular hydrogen. All single-determinant methods fail as bonds are stretched and electrons localize on distinct sites. Molecular hydrogen dissociates into an open-shell biradical (two H atoms). The molecular energy as a function of separation is given in Fig 6 of Ref. [4]. That figure also shows the failure of LDA, with a Coulson-Fischer point [212] $R_{CF} = 3.53$, where the unrestricted broken symmetry solution becomes lower in energy than the spin-singlet within LDA. In Fig 4.10, we show the error in the energy curve, using pure PPW's, and also separating into separate cells, using $\Delta = 1$ and $\eta = 10^{-4}$.

Beginning with the PPW's (dashed lines), we see that increasing J improves accuracy systematically, as expected. Moreover, for a given J = 1 or higher, we see that the error increases systematically as the bond is stretched until R_{CF} is reached. This is because the LDA orbital is becoming less and less close to the exact natural orbital as the bond is stretched. Beyond this point, there is a great decrease in error, as the the number of LDA orbitals doubles (due to spin-symmetry breaking). Even the largest PPW basis shown here (J = 2) does not achieve chemical accuracy close to the CF point. But our WLO's *do* reach chemical accuracy everywhere for J = 2, and almost everywhere with J = 1, using $3 \times 2 = 6$ functions for $R < R_{CF}$, and double that beyond. (The wavelet localization does not throw out any WLO's here.) Thus our basis set works, even through the CF point. Of course, in practice, quantum chemists want forces, and some smoothing procedure would be adopted to avoid the kink at the CF point.

The strong changes with R in the error in the red curve past the CF point can be attributed to the grouping of the scaling and wavelet functions. As the bond is stretched, because the functions are fixed in real space, some of the functions are assigned to the left cell, and others to the right. This assignment can change suddenly, causing a drop in the eigenvalue weights in the covariance matrix of one of the cells and decreasing the number of functions. Note that this effect occurs only for errors far below the chemical accuracy threshold.

Next we consider performance for longer chains of H atoms. Now the covariance cutoff becomes important for curtailing the total number of functions. Figure 4.11 illustrates the effect of the covariance cutoff for H₄ near equilibrium. The higher the value of η , the more functions are thrown away, but the greater the error is. If η is set too small, then no functions are removed, not even those that have essentially no effect on the energy. The figure shows that the full basis has an error of about 0.1 kcal/mol. But chemical accuracy is achieved with $\eta = 10^{-3}$ and only 14



Figure 4.11: Finite-basis energy error as a function of covariance cutoff η for H₂ at R = 2 with $J = \Delta = 1$. Without cutoff, there are 24 functions in the basis. The integer near each point is the number of functions in the basis.

functions. This is to be contrasted with $M_{no} = 6$ from Fig 4.3 and $M_{PPW} = 14$ from Fig 4.7. In this case (near equilibrium), the WLO's form a near-complete localized orthogonal basis with no more functions than PPW, and with lower error. Note that setting $\eta = 10^{-4}$ does not add in any more functions.

To see the effect as a function of bond length, in Table 4.1, we give energy errors and numbers of basis functions for various values of R and several values of Δ , for a J = 1 calculation with $\eta = 10^{-4}$. (In all cases, J = 0 was found to yield errors higher than 1 kcal/mol.) We see that the least number of functions needed occurs for $\Delta = 1$, especially as the chain is stretched.

Finally, we have run examples of 10-atom chains. We achieve chemical accuracy for J = 1, $\Delta = 1$ throughout the range of R shown in the table, with about 5 functions per site when $\eta = 10^{-4}$. This may seem like a large number of functions, but keep in mind that, as R increases, this is a strongly correlated system tending toward its thermodynamic limit. Moreover, we have required our total energy to be accurate to 1 kcal/mol all along the curve, not just the energy per atom.

R	2		3		4		5		6	
Δ	N_f	ΔE								
0.5	16	0.24	16	0.33	26	0.11	24	0.09	23	0.21
1.0	14	0.43	16	0.26	24	0.15	22	0.11	22	0.16
2.0	16	0.37	15	1.50	28	0.04	25	0.08	24	0.15
4.0	18	0.34	18	0.52	29	0.04	25	0.10	25	0.17

Table 4.1: WLO (J = 1) errors for H₄ as a function of separation, for various values for Δ . Chopping the PPW's yields up to 48 functions, but setting $\eta = 10^{-4}$ as the covariance cutoff yields the number of functions and accuracy shown.

R	1		2		3		4	
η	N_f	ΔE						
10 ⁻⁴	42	0.47	51	0.10	50	0.63	49	0.25
10 ⁻³	42	0.47	43	1.29	49	1.08	40	0.83

Table 4.2: Same as Table 4.1, but for H_{10} , with $J = \Delta = 1$, and two different covariance cutoffs.

One would also expect most energy differences to converge more rapidly than the total energy. Table 4.2 also illustrates the benefits of the covariance cutoff. By setting its value to 10^{-3} , we significantly reduce the number of functions as *R* increases, but in the middle, our error is slightly greater than 1 kcal/mol. For many practical purposes, this should be sufficient, but the larger lesson is that, for any desired application, there is a controllable trade-off between accuracy and number of functions.

We end with a heteronuclear diatomic, LiH, to show that our method still works in the absence of left-right symmetry. Fig. 4.12 was calculated with $J = \Delta = 1$ and $\eta = 10^{-4}$. The LDA orbitals remain an excellent starting point for approximating the NO's, and the NO's in the WLO basis are identical (on this scale) to the exact NO's. The energy error is only 1.04, using 11 basis functions.



Figure 4.12: The first two natural orbitals for stretched LiH (X's denote nuclear centers with Li on right). The exact NO's are marked in red, and are indistinguishable from the WLO NO's ($\Delta = J = 1$, $\eta = 10^{-4}$), black dotted line, but slightly different from the occupied LDA orbitals (green). Also shown are WLO's with weights above 10^{-4} (dashed lines). The WLO basis has 11 functions, and an error of 1.04 kcal/mol.

4.6 Discussion and conclusions

We have presented algorithms to generate a basis set that is adapted to a specific molecular system and designed to be used in correlated calculations. The basis begins with an inexpensive DFT or HF calculations, and the generation of additional functions from the occupied orbitals to allow correlation is even less expensive. A product plane wave (PPW) ansatz adds additional functions using a product of low momentum plane waves times each occupied orbital. In our 1D test systems, this ansatz produces results within chemical accuracy using about twice as many functions as in an ideal natural orbital basis. Then, to generate basis functions localized near each atom, we introduced a wavelet localization procedure. Compared to standard localization methods, which involve an orthogonal transformation of the existing functions without expanding the basis, wavelet localization produces stronger localization with much smaller orthogonalizing tails, at the expense of adding basis functions. This procedure is particularly useful for DMRG calculations, where locality in the basis is an important criteria. It may also improve scaling on large systems in other correlation approaches. Our method, as presented here, should allow much larger systems to be treated than previously possible in our 1D mimic of realistic electronic structure (such as the 100-atom chains of Ref. [36]).

Our procedure has only been given and tested upon a 1D mimic of the 3D world. A naive generalization of PPW to arbitrary 3D problems would involve many more plane waves, roughly the cube of the number in 1D. For a fixed momentum cutoff the number of plane waves also grows with the length of the system, even in 1D. This would appear to generate far too many functions to be practical, but the wavelet localization would counteract this effect. We can think about how this works by considering one particular cell, centered on an atom. The PPW basis generates occupied orbitals times plane waves with a low momentum cutoff. The number of functions needed to span this set in one cell should not be too large, since the only high frequencies present are from the cusps of the occupied orbitals at the nuclei, which in a Gaussian basis can be represented by a small number of basis functions. Otherwise, there are only a limited number of low frequency modes in a single atom cell. This means that there must be significant redundancy in the PPW functions, particularly for many electrons. The principle component analysis of the wavelet localization would remove this redundancy. This makes it clear that except for very small molecules, one should not apply PPW on its own, but in conjunction with wavelet localization. Nevertheless, there are likely significant challenges in going to 3D which we must leave for future work. In 1D, our bases give chemical accuracy with only about twice as many functions as in an equivalent natural orbital basis. It seems reasonable that a variation of our 1D approach can be found for 3D which is similarly less efficient than a natural orbital basis by only a modest factor.

One improvement to our PPW approach which we have not explored here is to give more weight to the occupied orbitals than to the additional functions coming from the plane waves with nonzero momentum. This would be fairly simple to implement in our wavelet localization, by multiplying the J > 0 functions by a weighting factor less than 1. One would expect this natural modification to further reduce the number of functions needed for chemical accuracy. We also note that our procedure could also be applied without chopping, but still removing irrelevant basis functions, by constructing the orthonormal basis from the PPW's

$$g_j^i = \sum_k O_{jk}^{-1/2} f_k^i, \tag{4.10}$$

where *O* is the overlap matrix of the f^i . Now $\rho^c = O$, so the principle component analysis consists of forming a basis of the eigenvectors of the overlap matrix with the largest eigenvectors, up to cutoff η . This procedure reduces basis-set linear dependence; here it might reduce the PPW basis size significantly without much loss of accuracy.

A number of existing approaches also utilize or are based on approximate natural orbitals. For example, some Gaussian basis sets attempt to reproduce properties of atomic natural orbitals [213]. A key difference with our approach is that we start from the beginning with orbitals adapted to the specific molecule under consideration, based on a DFT or HF calculation. It would be interesting to compare the number of functions needed to reach chemical accuracy in 3D between our PPW approach and standard Gaussian basis sets. (We do not have these Gaussian basis sets for our 1D test systems.)

Another common approach is to find approximate natural orbitals from a low-order correlation calculation, such as second order perturbation theory, e.g. MP2 [214]. Our PPW method is simpler and faster, and it would be interesting to compare the accuracy of these two approaches. One might also combine them: in cases where the perturbation calculation was expensive to do in a large basis, one might first get a PPW basis, which would be much smaller than an unadapted basis, and then refine it further by getting approximate natural orbitals with a perturbation theory approach.

The localization using wavelets could be applied in a broader context than we have used here, such as to standard Gaussian bases or to approximate natural orbitals coming from a low order correlation method. This could potentially improve the performance of DMRG or other tensor network methods. By improving the sparsity of the Hamiltonian, it may also improve the computational scaling for DFT on large systems. In particular, using wavelet localization to impose locality only at the atomic level may be more efficient than existing wavelet approaches which do not recombine the wavelets into a smaller number of functions. Specifically, one could wavelet filter a standard Gaussian basis to produce an orthogonal basis with more locality and sparsity than traditionally localized Gaussian bases.

Since we are trying to produce basis sets for correlated calculations, where basis set convergence is slower than for DFT or HF calculations, we must think about the effect of the basis on the electron-electron cusp. Our choice of 1D potential interaction, which has a slope discontinuity at the origin, is designed to partially mimic the electron-electron cusp behavior in 3D. In 3D, the potential diverges as $r \rightarrow 0$, but the effect is substantially reduced by the 3D volume element. The moderate singularity we have in 1D is similar, but we cannot expect our results to match 3D precisely. Also, when trying to achieve chemical accuracy, the short range cusp behavior is thought to be less relevant than intermediate distance electron-electron correlation. This further complicates the comparisons between 1D and 3D, and a 3D procedure and benchmark calculations are clearly needed.

Another difficulty in implementing our approach in 3D is the computation of the integrals defining the Hamiltonian, once the basis is defined. In our 1D implementation, all integrals are written in terms of sums over the fine grid; this would not be practical in 3D. Wavelet bases, which are a crucial part of our wavelet localization, are able to represent nuclear cusps more efficiently than grids, so one might try to work directly in the wavelet basis, expressing all the final basis functions as linear combinations of wavelet functions [152, 157, 177]. However, wavelets are much less efficient than atom-centered Gaussians for representing nuclear cusps, and so a much more efficient approach might be to try to combine wavelets with a few Gaussians per nucleus. Another approach to dealing with nuclear cusps would be to use pseudopotentials, so there are no cusps. Yet another

is to employ a basis set that inherently has a one dimensional structure[204, 215, 216, 217] We leave this set of 3D implementation problems for future work.

4.7 Supplemental Information

We point out that the form of our density matrix for the partitioned wavelet basis has the form

$$\hat{\rho} = \bigoplus_{k=1}^{N_a} \check{\rho}_k^c = \begin{pmatrix} \check{\rho}_1^c & 0 & 0 & 0 & \dots \\ 0 & \check{\rho}_2^c & 0 & 0 & \dots \\ 0 & 0 & \check{\rho}_3^c & 0 & \dots \\ 0 & 0 & 0 & \check{\rho}_4^c & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$
(4.11)

We did investigate what happens if we project our scaling functions from each of the boxes individually. This causes each of the sub-density matrices for each atomic region to have the form

$$\check{\rho}_k^c = \check{\Lambda} \oplus \check{1}_S \tag{4.12}$$

where $\check{1}_S$ is an identity matrix of dimension of the number of scaling functions. $\check{\Lambda}$ represents the sub-density matrix formed by the remaining vectors.

However, adding scaling functions in this manner did not improve the energy appreciably or fast enough. In general, the best combination was $\Delta = J = 1$.

Chapter 5

Kohn–Sham calculations with the exact functional

5.1 Overview

As a proof of principle, self-consistent Kohn–Sham calculations are performed with the *exact* exchange-correlation functional. Finding the exact functional for even one trial density requires solving the interacting Schrödinger equation many times. The density matrix renormalization group method makes this possible for one-dimensional, real-space systems of more than two interacting electrons. We illustrate and explore the convergence properties of the exact KS scheme for both weakly and strongly correlated systems. We also explore the spin-dependent generalization and densities for which the functional is ill defined.

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5.2 Introduction

Four score and seven years ago, our physics forebears [66, 67] brought into this world a new theory, conceived in simplicity, and dedicated to the proposition that although all particles are waves [218], their density can be simply calculated [66, 67]. Now we are engaged in a great electronic structure debate, testing whether Kohn–Sham theory [39], or any density functional theory [1] so conceived and so dedicated, can endure in the face of strongly correlated systems. We have come to dedicate a portion of this paper, as a final convergence proof [37] for those who have dedicated their lives to developing the constrained search [219] and approximations thereto [220, 221, 222]. It is altogether fitting and proper that we should prove this.

Kohn–Sham (KS) [39] density functional theory (DFT) is now a widely used electronic structure method, attaining useful accuracy with present approximations [40]. The method finds the ground-state energy of a many-electron, interacting system by solving an effective non-interacting problem. This non-interacting problem must be solved self-consistently, because its potential (the KS potential) is a functional of the electron density. The most vital piece of this KS potential is derived from the mysterious exchange-correlation functional, which can be computed exactly with great cost [112, 223]. This exact functional provides the formal foundations of KS-DFT for all electronic systems (with some caveats) [219]. However, the utility of KS-DFT derives from simple and computationally efficient approximations to the exchange-correlation (XC) energy [220, 221, 222] which can be surprisingly reliable and usefully accurate for broad classes of systems, yet fail badly for others.

Traditionally, study of the exact XC energy functional focused on finding general exact properties that can either be built into approximations, or used to understand their failures [72, 222, 224, 225]. In studying the exact theory, we learn what is and is not reproduced by the exact functional; e.g. that the HOMO-LUMO gap of the KS system is not equal to the fundamental (charge) gap of the system [226, 227]. As computational power and algorithms evolved, it also became possible to

take a highly accurate solution of the Schrödinger equation, extract the ground-state density, and find the exact KS potential for the system of interest, notably for few electron systems [27, 35, 228, 229, 230, 231, 232, 233, 234, 235]. These *inversions* are often quite demanding, since all quantities must be sufficiently accurate to extract the small differences in energies and potentials that form the various components of exchange and correlation.

But even such heroic efforts do *not* produce a way of solving the KS equations with the exact XC functional. This is because, in an actual KS calculation, the XC functional is needed not just for the ground-state density of the system to be solved, but for a sequence of trial densities that ultimately converges to the solution for that problem. To find the XC functional for some trial density, one must solve the Schrödinger equation for the potential for which that density is the ground state, both for interacting and non-interacting electrons. Worse still, these potentials are a priori unknown. Advancing just one step in the KS calculations thus requires solving many interacting electronic problems in order to *find* the right potential that yields the trial density. We call this an interacting inversion, and previous examples have been limited to 2 electrons [223, 236, 237].

In this paper, we detail how to find the exact XC functional for realistic models of electrons in one dimension. By realistic, we mean models whose properties mimic those of real systems, and whose treatment with approximate density functionals yields results similar to those for real systems [35]. We use the density matrix renormalization group [238, 239, 240] to solve the Schrödinger equation, because of its tremendous efficiency for one-dimensional (1d) systems. In Ref. [37], we used this capability to explore the convergence of a simple algorithm for the KS scheme, ultimately proving that, no matter how strongly correlated, convergence can always be achieved in a finite number of iterations. Various approximate functionals have their own convergence proofs [241?], but here we detail exactly how the exact calculations are done, and test further properties of the exact functional.

5.3 Background

Typical solid state and quantum chemistry investigations into electronic structure begin with the non-relativistic continuum Hamiltonian in the Born–Oppenheimer approximation,

$$\hat{H} \equiv \hat{T} + \hat{V} + \hat{V}_{ee}$$

$$\equiv \sum_{i=1}^{N} \left(-\frac{1}{2} \nabla_i^2 + v(\mathbf{r}_i) \right) + \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$
(5.1)

which describes the quantum behavior of N electrons in an external potential $v(\mathbf{r})$ determined by the (classical) nuclei via the operators: the electron kinetic energy \hat{T} , their potential energy \hat{V} , and the electron-electron interaction \hat{V}_{ee} . The eigenstates Ψ_j and eigenvalues E_j (the energies) of the Hamiltonian \hat{H} determine all the properties of the system.

Despite Eq. (5.1) being the key to everyday electronic structure, an accurate solution for even the ground-state energy E and wavefunction Ψ is not presently tractable for large molecules. This problem continues to inspire the development of new approximations and methods to solve the many-body problem. Some methods—such as Hartree–Fock theory [242], quantum Monte Carlo [243], and coupled cluster [242]—attempt to approximate, sample, or construct the wavefunction. Density functional theory, on the other hand, approaches the many-body problem quite differently.

While Ψ allows one to characterize the system completely, the much simpler ground-state electron density $n(\mathbf{r})$ was proven by Hohenberg and Kohn (HK) to also determine all the properties of the system [1]. Their theorem allows us to formally work with the density as the basic variable instead of the wavefunction [219]. The keystone of this far-reaching proof is the one-to-one correspondence between the ground-state density $n(\mathbf{r})$ and the potential $v(\mathbf{r})$ of a system, which characterizes the system completely. This one-to-one mapping will be explored in greater detail in Sec. 5.4, since it is crucial for calculate the exact functional.

As an important mathematical aside, the potential corresponding to a given density is unique if it exists, but there are some densities $n(\mathbf{r})$ which are not *ensemble v-representable*, i.e. not the ground states of any potential $v(\mathbf{r})$ [244]. We explore this complication later, in Sec. 5.5.7.

A simple corollary of the HK theorem is that the ground-state energy of a system can be determined by minimizing over trial electron densities [1]

$$E_v = \min_n E_v[n] \tag{5.2}$$

$$E_{v}[n] \equiv F[n] + \int d^{3}r n(\mathbf{r}) v(\mathbf{r}), \qquad (5.3)$$

where F[n] accounts for the electronic kinetic energy and electron-electron repulsion energy, and is universal, i.e., independent of the external potential $v(\mathbf{r})$. When degeneracy is not an issue [245], the functional F[n] can be found by minimizing the expectation value of $\hat{T} + \hat{V}_{ee}$ over all properly antisymmetric wavefunctions Ψ that yield the density $n(\mathbf{r})$ [112, 219]:

$$F[n] = \min_{\Psi \to n} \langle \Psi | \{ \hat{T} + \hat{V}_{ee} \} | \Psi \rangle, \tag{5.4}$$

and the minimizing Ψ is denoted $\Psi[n]$. This is the *pure-state* formulation of DFT. The generalization for degenerate systems involves replacing the expectation value in Eq. (5.4) with a trace over the ground-state ensemble Γ [219]. The only known way to exactly calculate the functional thus implicitly requires use of a wavefunction (or a density matrix for degenerate systems).

We now turn to the formulation of the most popular of DFT implementations, Kohn–Sham DFT [39]. Kohn–Sham theory creates a doppelgänger of the interacting system: a set of non-interacting electrons with the same density. This non-interacting system, the KS system, is characterized by its potential, $v_s[n](\mathbf{r})$, defined implicitly so that a system of N non-interacting electrons in this potential has density $n(\mathbf{r})$. This means that after solving the non-interacting Schrödinger (i.e. KS)

equation and obtaining the KS orbitals $\phi_i(\mathbf{r})$ (in Hartree units):

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm s}[n](\mathbf{r})\right\}\phi_j(\mathbf{r}) = \varepsilon_j\phi_j(\mathbf{r}).$$
(5.5)

One finds the density $n(\mathbf{r})$ by occupying the N/2 lowest-energy orbitals,

$$n(\mathbf{r}) = 2\sum_{j=1}^{N/2} |\phi_j(\mathbf{r})|^2$$
(5.6)

(where for simplicity we assume that the system is spin-unpolarized). Obtaining the KS potential $v_{\rm S}[n](\mathbf{r})$ for a density $n(\mathbf{r})$ is an inverse problem, on a firm foundation through the HK theorem applied to non-interacting systems. (Some densities, however, will prove to be non-*v*-representable [246], so the potential $v_{\rm S}[n](\mathbf{r})$ is unique, up to a constant, but only if it exists.) Many algorithms to invert a density to find its KS potential have been suggested [229, 231, 234, 247, 248, 249, 250]; ours will be described in Sec. 5.4.

As a descendent of DFT, Kohn–Sham DFT determines the energy of a system by knowledge of the density alone. Within the KS framework, the universal functional F[n] is written as

$$F[n] = T_{\rm S}[n] + U[n] + E_{\rm XC}[n]$$
(5.7)

where $T_{\rm S}[n]$ is the kinetic energy of the KS orbitals:

$$T_{\rm S}[n] \equiv -\sum_{j=1}^{N/2} \int d^3r \,\phi_j^*(\mathbf{r}) \nabla^2 \phi_j(\mathbf{r}), \qquad (5.8)$$

U[n] is the Hartree energy:

$$U[n] \equiv \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$
(5.9)

and $E_{\rm XC}[n]$ is the exchange-correlation (XC) energy, defined by Eq. (5.7). Very successful (albeit

crude) approximations to $E_{\rm xc}[n]$ have been developed [220, 221, 222], which make KS theory a standard and practical approach to electronic structure. Our work focuses on the exact $E_{\rm xc}[n]$, with a few comparisons to the simplest density functional approximation, the local density approximation (LDA) [220].

The KS framework offers a convenient way to minimize $E_v[n]$ as in Eq. (5.2), by solving noninteracting systems with an effective potential. We guess an input density $n_{in}^{(i)}(\mathbf{r})$ and use it to calculate a trial KS potential $v_s^{(i)}(\mathbf{r})$:

$$v_{\rm S}^{(i)}(\mathbf{r}) = v(\mathbf{r}) + v_{\rm H}[n_{\rm in}^{(i)}](\mathbf{r}) + v_{\rm XC}[n_{\rm in}^{(i)}](\mathbf{r}), \qquad (5.10)$$

where $v_{\rm H}[n](\mathbf{r}) = \delta U[n] / \delta n(\mathbf{r})$ is the Hartree potential:

$$v_{\rm H}[n](\mathbf{r}) = \int d^3 r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},\tag{5.11}$$

and $v_{\rm XC}[n](\mathbf{r}) = \delta E_{\rm XC}[n]/\delta n(\mathbf{r})$ is the XC potential. The Hartree and XC potentials together account for two-body interactions [34], and are found by taking functional derivatives of their parent energy functionals.

After calculating $v_s^{(i)}(\mathbf{r})$ for the given input density, we solve the trial KS system (i.e. Eq. (5.5) with our trial KS potential) to obtain an output density $n_{out}^{(i)}(\mathbf{r})$. If the output density equals the input density, we have achieved self-consistency and have found a stationary point of $E_v[n]$. This may be quantified by calculating a simple criterion for convergence:

$$\eta^{(i)} \equiv \frac{1}{N^2} \int d^3r \left(n_{\text{out}}^{(i)}(\mathbf{r}) - n_{\text{in}}^{(i)}(\mathbf{r}) \right)^2, \tag{5.12}$$

declaring the calculation converged when $\eta^{(i)} < \delta$, If the calculation has not converged, a new guess density $n_{in}^{(i+1)}(\mathbf{r})$, such as $n_{out}^{(i)}(\mathbf{r})$, is plugged into Eq. (5.10) for the next iteration, and we repeat until converged. For the exact XC functional, the converged density is the ground-state



Figure 5.1: The KS scheme.

density of interacting electrons in the potential $v(\mathbf{r})$ [37]. This iterative-convergence procedure is known as the KS scheme [251], and is illustrated in Fig. 5.1. The possibility of finding other stationary points besides the ground-state for the exact functional will be addressed in Sec. 5.5.

The Kohn–Sham DFT approach to electronic structure thus converts the many-body problem into a non-interacting problem which must be solved self-consistently. The exact procedure requires finding the many-body system with a given density, with wavefunction $\Psi[n]$, to determine $E_{\text{XC}}[n]$ and $v_{\text{XC}}[n](\mathbf{r})$, and thus is as costly as solving the original many-body problem (see Sec. 5.5). However, the KS scheme would be neither useful nor practical at such a computational cost. Evaluating $v_{\text{XC}}[n](\mathbf{r})$ at each iteration of the KS scheme is (usually) a trivial and inexpensive step with present approximations, since the functional derivative is known explicitly.

5.4 Inversions

Inverting a density $n(\mathbf{r})$ to find its KS potential $v_{\rm S}[n](\mathbf{r})$, or to find its external potential $v[n](\mathbf{r})$ (for real, interacting electrons) is not a straightforward task. In this section we discuss how to do this for an arbitrary *v*-representable density. As a by-product of these inversions, we obtain the implicitly defined KS orbitals and interacting wavefunction $\Psi[n]$, which allow us to evaluate the XC potential and energy in Sec. 5.5.

Non-interacting inversions are performed to find the KS potential of exact densities for a variety of systems [27, 35, 232]. The notation we use for the potential corresponding to the density $n(\mathbf{r})$ of non-interacting electrons is $v_s[n](\mathbf{r})$, which we have already seen in Eq. (5.5). This inversion is a simple matter for one or two electrons with opposite spins, since the KS equation can be rearranged to obtain:

$$v_{\rm S}[n](\mathbf{r}) = \frac{1}{2} \frac{\nabla^2 \sqrt{n(\mathbf{r})}}{\sqrt{n(\mathbf{r})}} + \varepsilon, \quad (N \le 2)$$
(5.13)

where ε is a constant (the only occupied KS eigenvalue). For more electrons, one can use an iterative procedure to determine $v_{\rm s}[n](\mathbf{r})$. Initially a potential $v_{\rm s}^{(1)}(\mathbf{r})$ is guessed, e.g. Eq. (5.13). Then, starting with i = 1:

- 1. For the potential $v_s^{(i)}(\mathbf{r})$, solve the non-interacting Schrödinger equation for orbitals $\phi_j^{(i)}(\mathbf{r})$, doubly-occupying to obtain the density $n^{(i)}(\mathbf{r})$.
- 2. If $n^{(i)}(\mathbf{r})$ is within tolerance of $n(\mathbf{r})$, we are done, i.e. $v_s^{(i)}(\mathbf{r}) = v_s[n](\mathbf{r})$ and $\phi_j(\mathbf{r}) = \phi_j^{(i)}(\mathbf{r})$. Otherwise, continue.
- 3. A new potential $v_s^{(i+1)}(\mathbf{r})$ is chosen, based on how different $n^{(i)}(\mathbf{r})$ is from $n(\mathbf{r})$. Roughly speaking, where $n^{(i)}(\mathbf{r})$ is too low, the new potential $v_s^{(i+1)}(\mathbf{r})$ is lowered from the old $v_s^{(i)}(\mathbf{r})$, and where $n^{(i)}(\mathbf{r})$ is too high, the new potential is raised.

4. Increment *i* and repeat steps 1 to 4.

The only difference between different inversion algorithms is how the new potential is determined in step 3. The problem can be reduced to finding the root of a nonlinear function of many variables, which can be treated at various levels of sophistication [252]. We discuss Broyden's method at the end of this section. With the KS potential $v_s[n](\mathbf{r})$ and orbitals $\phi_j(\mathbf{r})$, we can evaluate functionals such as $T_s[n]$ using Eq. (5.8).

Interacting inversions are rarely done, since they are far more expensive than non-interacting inversions, and require solving the many-body problem many times. Only two-electron problems have been studied, in one case to understand the adiabatic approximation within TDDFT [236, 237] and in another to study the self-interaction error within LDA [223]; though we have recently studied four-electron systems [37]. The potential $v[n](\mathbf{r})$, which corresponds to the interacting system of electrons with density $n(\mathbf{r})$, can be found using the same algorithm as for $v_{\rm s}[n](\mathbf{r})$, though in step 1 we must solve an interacting problem for the many-body wavefunction $\Psi^{(i)}$ rather than the noninteracting Schrödinger equation for orbitals $\phi_j^{(i)}(\mathbf{r})$. At the end of the inversion we obtain $\Psi[n]$, the wavefunction which minimizes F[n] in Eq. (5.4), allowing us to compute F[n] for that specific density.

To illustrate the theory behind KS-DFT, we solve interacting systems using the density matrix renormalization group (DMRG) [238, 239], which is the most efficient wavefunction solver in 1d, capable of handling both strong and weak correlation. We apply DMRG to model 1d continuum systems by discretizing space into N_g grid points with a small grid spacing Δ [35, 36]. With this method, we can invert 1d systems with over 100 electrons [36]. For our model systems we employ a softened Coulomb interaction between electrons [12, 33, 35, 36, 236]:

$$v_{\rm ee}(u) = 1/\sqrt{u^2 + 1}.$$
 (5.14)



Figure 5.2: Density inversion of arbitrary 4-electron density for non-interacting and interacting potentials. Solving either the interacting Schrödinger equation in the potential v[n](x) or solving the non-interacting Schrödinger equation in the potential $v_s[n](x)$ yields the density in the top panel.

Figure 5.2 shows a four-electron example of an interacting inversion ¹. For some arbitrary density like this one (meaning a density we would not find in nature), we want to find the associated KS and interacting potentials. This is the problem we encounter during the self-consistent calculation of the KS equations. Since we ultimately find $\Psi[n]$ at the end of the inversion, we can evaluate F[n] (given soft-Coulomb interactions); likewise with $\phi_j(\mathbf{r})$ we can obtain $T_s[n]$. For the example density of Fig. 5.2 we find F[n] = 3.07, $T_s[n] = 0.843$, U[n] = 3.628, so $E_{xc}[n] = -1.397$. The XC energy is thus calculated using simple energy differences; and we obtain the XC potential in the same way. We further describe these matters in the next section.

To close this section, we describe our recipe for step 3 of the inversion algorithm. The idea is to build an approximation for the density-density response matrix, χ , which determines how a small

¹The density shown in Fig. 5.2 is given by $\tilde{n}(x) = e^{x/15-x^2/2+x^4/20-x^6/750}$, divided by a normalization factor such that it contains four electrons.

change in the potential will change the density:

$$\int d^3 r' \chi(\mathbf{r}, \mathbf{r}') \,\delta v(\mathbf{r}') = \delta n(\mathbf{r}).$$
(5.15)

Restricting our attention to 1d, we recast this equation as the matrix equation $\chi \, \delta v = \delta n$, where χ is an (unknown) $N_g \times N_g$ matrix, and δv , δn are vectors with N_g components, where N_g is the number of grid-sites in the system. A constant change in the potential (i.e. $\delta v = c_1$) will give zero change in the density ($\delta n = 0$), and a constant change in the density ($\delta n = c_2$) is impossible, since N is fixed. Therefore we consider orthonormal basis functions for changes in the potential and density which integrate to zero, encoded as columns in the matrices W and M, respectively [253]. Within this basis, the density-density response matrix can be approximated by a smaller matrix, A:

$$\chi \approx MAW^T. \tag{5.16}$$

This factorization of the matrix χ looks very much like (and is inspired by) the singular value decomposition (SVD) of χ , which would give an exact breakdown of χ into optimal bases M and W, with A being diagonal. We do not know χ a priori, but an approximation to χ (or A) can be iteratively improved using a quasi-Newton method (we use Broyden's method from Ref. [254]). We construct appropriate basis vectors for M and W using orthonormalized differences of trial densities from the target density. As A is refined, the bases M and W can be optimized (if desired) by computing the SVD of A, a procedure which is also useful to compute A^{-1} , and thus χ^{-1} . The next trial potential for step 3 is determined by: $v^{(i+1)} = v^{(i)} + \chi^{-1}(n - n^{(i)})$. Typically around 20 basis vectors in M and W are required to obtain a trial density indistinguishable from the target density on the scale of Fig. 5.2.

5.5 Results

We have now sufficient machinery to calculate the exact exchange-correlation energy and potential for any trial density, as encountered in the KS scheme. For convenience, we define $E_{\text{HXC}}[n] \equiv U[n] + E_{\text{XC}}[n]$, which can be evaluated (using Eqs. (5.4) and (5.7)) as:

$$E_{\rm HXC}[n] = \langle \Psi[n] | \{\hat{T} + \hat{V}_{\rm ee}\} | \Psi[n] \rangle - T_{\rm s}[n].$$
(5.17)

From Section 5.4, we know how to obtain $\Psi[n]$ and $T_{s}[n]$ using inversions. Therefore the exact $E_{xc}[n]$ is no obstacle in principle, but extremely computationally expensive in practice. Similarly, the HXC potential is:

$$v_{\text{HXC}}[n](\mathbf{r}) = v_{\text{S}}[n](\mathbf{r}) - v[n](\mathbf{r}), \qquad (5.18)$$

which are available from interacting and non-interacting inversions. The construction of the exact functional using inversions is illustrated in Fig. 5.3.

To algorithmically implement the KS scheme, we must choose our input densities $n_{in}^{(i)}(\mathbf{r})$ for each iteration *i*; each output density $n_{out}^{(i)}(\mathbf{r})$ is determined by solving the KS equations (5.5). Although more sophisticated algorithms are used in practice [241, 255, 256, 257, 258, 259?], we choose the simple algorithm given below. We emphasize that we make no claims as to the efficiency of this particular algorithm. We expect many other algorithms to be more efficient. But this simple choice allows a simple proof of convergence, and provides an initial framework to study convergence rate questions.

The first input density $n_{in}^{(1)}(\mathbf{r})$ is arbitrarily chosen. The subsequent input densities are calculated via the linear density mixing algorithm,

$$n_{\rm in}^{(i+1)}(\mathbf{r}) = (1-\lambda) n_{\rm in}^{(i)}(\mathbf{r}) + \lambda n_{\rm out}^{(i)}(\mathbf{r}), \qquad (5.19)$$



Figure 5.3: To determine the $E_{\text{HXC}}[n]$ and $v_{\text{HXC}}[n](\mathbf{r})$: Our exact calculation requires a computationally demanding inversion algorithm to find the one-body potential $v[n](\mathbf{r})$ of the interacting system whose density is $n(\mathbf{r})$, with KS orbitals $\phi(\mathbf{r})$, in addition to a non-interacting inversion to find $v_{\text{S}}[n](\mathbf{r})$. In case of degeneracy, mixed-states should be used instead of pure-state wavefunctions in both non-interacting and interacting inversions. The right hand side differs from the left in that it describes an interacting inversion.

where λ is a parameter between 0 and 1, which aids convergence. At $\lambda = 1$, no density mixing is performed, and the output density of iteration *i* is used as the input for iteration *i* + 1. While this might allow for quick convergence, there is the danger of repeatedly overshooting the ground-state density and not converging. If this happens, smaller steps must be taken, i.e. small λ ($\lambda = 0$ not allowed) must be used. These convergence issues are discussed more thoroughly in Sec. 5.5.2, where we investigate how small this density mixing λ needs to be in order to converge the calculation.

5.5.1 Illustration

In this section we use the exact functional within the KS scheme for a model one-dimensional continuum system, demonstrating convergence to the true ground-state density. We also explain why the only stationary point of the exact functional is the true ground-state density.

In our model one-dimensional system, electrons are attracted to the nuclei via the potential [35]

$$v_{\text{e-nuc}}(x) = -1/\sqrt{x^2 + 1},$$
 (5.20)

and electrons interact with the corresponding repulsive potential as already mentioned via Eq. (5.14).

In Fig. 5.4, we plot the trial densities and KS potentials for a four-electron, four-atom system. The interatomic spacing *R* is chosen to make correlations moderate. Choosing a density mixing of $\lambda = 0.30$ affords fairly rapid convergence. We find that the final density, calculated within our KS algorithm, is equal to the true ground-state density of the system. We plot the final converged KS, Hartree, and XC potentials in Fig. 5.5.

Regarding stationary points of the exact functional, we find that, in all the cases we ran, our KS algorithm converged to the true ground-state density. An analytic result confirms that, given *v*-representable densities, the only stationary point of the exact KS scheme is the ground-state density



Figure 5.4: KS procedure for a moderately correlated 4-electron system (four hydrogen atoms separated by an interatomic spacing of R = 3), using a fixed $\lambda = 0.3$ and showing the first few iterations of: (a) differences in the trial output densities from the ground-state density (shown in Fig. 5.5) and (b) trial KS potentials.



Figure 5.5: External, KS, Hartree, and XC potentials, as well as the ground-state density, for a moderately correlated 4-electron system (four hydrogen atoms separated by an interatomic spacing of R = 3).

of the system [260]. We can see this by plugging the exact $v_{\text{HXC}}[n](\mathbf{r})$ from Eq. (5.18) into the KS update (5.10). The exact scheme then proceeds as

$$v_{\rm s}(\mathbf{r}) := v_{\rm s}[n_{\rm in}](\mathbf{r}) + \left(v(\mathbf{r}) - v[n_{\rm in}](\mathbf{r})\right),\tag{5.21}$$

with self-consistency reached when $v(\mathbf{r}) = v[n_{in}](\mathbf{r})$. This occurs at precisely one density: at the ground-state density $n_{g.s.}(\mathbf{r})$, which is unique by the HK theorem. Thus the exact KS scheme has only one stationary point for *v*-representable densities.

In density functional theory, there is no guarantee that a KS potential exists for a given physical system. The guarantee is that if it does exist, it is unique and, as we pointed out above, the only stationary point of the KS equations. Densities with legitimate KS potentials are called non-interacting *v*-representable. We have performed many non-interacting inversions on accurate ground-state densities of atomic chains, and have always found their KS potentials to exist, even when the bond lengths are stretched. Since standard density functional approximations usually become inaccurate for strongly correlated systems, such as when bonds are stretched, a potential pitfall for KS-DFT is that such systems may fail to be non-interacting *v*-representable. While there are subtleties to identifying whether a density is *v*-representable or not (as discussed further in Sec. 5.5.7), *v*-representability does not appear to be the main issue when strong correlation is involved [261, 262, 263, 264]. Instead, good approximate functionals simply are missing at present [265, 266]. If *v*-representability were to blame, the entire KS apparatus, despite being exact in principle, could not be applied to such systems. Happily, our results show no evidence of such a disastrous situation.

5.5.2 First steps

Knowing that there is only one stationary point of the KS scheme (for *v*-representable densities) tells us nothing about the difficulty in finding it. In this section we consider the most basic part of

the KS scheme – a single step in the KS algorithm – which will help us understand the convergence behavior of the exact functional for different systems. We will see why strongly correlated systems are more difficult to converge than weakly correlated systems.

To explore how the KS scheme converges, we calculate the energy of the system which interpolates between the input and output densities for a single step of the algorithm, measured against the ground-state energy:

$$\Delta E(\lambda) = E_{\nu}[n_{\lambda}] - E_{\nu}, \qquad (5.22)$$

where $n_{\lambda}(\mathbf{r})$ linearly interpolates between the input density (at $\lambda = 0$) to the output density ($\lambda = 1$), just as in Eq. (5.19). We plot $\Delta E(\lambda)$ as well as the input, output, and exact densities for various systems in Figures 5.6 and 5.7. As can be seen, the output density is in the right direction to minimize $E_{v}[n]$, but it overshoots the minimum. Starting the next iteration of the KS scheme with this output density would not (in general) allow convergence; therefore a mixture of the input and output densities is used as the next input, thus motivating Eq. (5.19). The optimal mixing λ minimizes $E_{\nu}[n_{\lambda}]$ on the interval (0,1], and could be found using a line search. But even with the optimal mixing, neither of the chosen starting points (a non-interacting and a pseudouniform density) produces the ground-state density on the first iteration, so it takes a few iterations to converge. It is perhaps surprising, however, that a single iteration of the KS scheme could get so close to the ground state. For the weakly correlated system (Fig. 5.6), the non-interacting starting point gets within $\Delta E = 0.001$ of the ground-state energy with $\lambda = 0.45$, whereas the pseudouniform starting point minimizes $\Delta E = 0.004$ with $\lambda = 0.45$. For the strongly correlated system (Fig. 5.7), the optimal λ 's are smaller and the ΔE 's are larger: the non-interacting initial point minimizes at $\Delta E = 0.002$ with $\lambda = 0.44$, and the pseudouniform initial point minimizes ΔE at 0.094 around $\lambda = 0.21.$

Figures 5.6 and 5.7 each plot only two cuts through the infinite-dimensional functional landscape.



Figure 5.6: A single step in the KS scheme for a weakly correlated system (H₄ with R = 2) away from two different initial densities: non-interacting electrons in the external potential (NI) and a pseudouniform electron density (PU). These initial densities are the dashed curves in (a) and (b), and the solid curves are the output densities for each KS step; for comparison the dotted curve is the exact density. The lower panel plots Eq. (5.22), the energy of the system as it interpolates from the input to the output density.



Figure 5.7: A single step in the KS scheme for a strongly correlated system (H₄ with R = 4) away from two different initial densities: non-interacting electrons in the external potential (NI) and a pseudouniform electron density (PU). These initial densities are the dashed curves in (a) and (b), and the solid curves are the output densities for each KS step; for comparison the dotted curve is the exact density. The lower panel plots Eq. (5.22), the energy of the system as it interpolates from the input to the output density.

Figure 5.6 models a weakly correlated system—a four atom system with an interatomic spacing of R = 2—where a Slater determinant [267] of non-interacting electrons is a good approximation to the underlying wavefunction. But as we stretch the bonds to R = 4 for Fig. 5.7, strong static correlation arises, and the KS wavefunction is less like the true wavefunction of the interacting system than that of Fig. 5.6. Thus the density of a non-interacting system in the external potential is a poor start for the KS scheme, and energy differences from the ground-state are larger for the strongly correlated system than for the weakly correlated system. Besides the scale, one might ask how the functional landscape differs between strongly correlated systems and weakly correlated systems. While the two NI curves in Figures 5.6 and 5.7 are deceptively similar, the PU curves begin to reveal the treacherous landscape of the strongly correlated system near the minimum.

We now look at the second iteration of the KS scheme to see if there is a difference between the strongly and weakly correlated systems. We choose the NI-path density from Fig. 5.7 with a good (but not optimal) mixing of $\lambda = 42\%$ as input into the KS equations. For the weakly correlated system of Fig. 5.6, the second KS step (not shown) looks much like the first step, though with a much smaller energy scale involved. Thus a fairly large λ may be used when correlations are weak, and convergence is rapid. But it is not the same for the strongly correlated system. As shown in Fig. 5.8, the next iteration of the KS procedure will not allow us to make the same giant stride as in the first iteration. For the new λ -mixed density, we again evaluate $\Delta E(\lambda)$ from Eq. (5.22) and find that it reaches a minimum much sooner. Thus a much smaller λ —around 6% as seen in the inset—must be chosen in order not to go far off track. Furthermore, choosing even the optimal λ does not result in a much better energy as it did in the first iteration. This makes convergence a long and difficult process, since we can only afford to take small steps.

In the last part of this section, we give some formulas which may aid in determining the optimal λ each step. We consider derivatives of $E_v(\lambda) \equiv E_v[n_\lambda]$ with respect to λ . For example, large $E_v''(\lambda) \equiv d^2 E_v[n_\lambda]/d\lambda^2$ relative to the magnitude of $E_v'(\lambda) \equiv dE_v[n_\lambda]/d\lambda$ requires a smaller λ to lower the energy. Given some bound on $E_v''(\lambda)$, one could analytically determine a safe (i.e. not

too large or too small) approximation to the optimal λ [268]. The derivatives of $E_{\nu}(\lambda)$ may be taken analytically [37, 269]:

$$E_{\nu}'(\lambda) = \int d^{3}r \frac{\delta E_{\nu}[n]}{\delta n(\mathbf{r})} \Big|_{n_{\lambda}(\mathbf{r})} \left(n_{1}(\mathbf{r}) - n_{0}(\mathbf{r}) \right) = \int d^{3}r \left(\nu(\mathbf{r}) + \nu_{\text{HXC}}[n_{\lambda}](\mathbf{r}) - \nu_{\text{S}}[n_{\lambda}](\mathbf{r}) \right) \left(n_{1}(\mathbf{r}) - n_{\delta}(\mathbf{r}) \right) \\ E_{\nu}''(\lambda) = \int d^{3}r \int d^{3}r' \left(n_{1}(\mathbf{r}) - n_{0}(\mathbf{r}) \right) \left(f_{\text{HXC}}[n_{\lambda}](\mathbf{r}, \mathbf{r}') - \chi_{\text{S}}^{-1}[n_{\lambda}](\mathbf{r}, \mathbf{r}') \right) \left(n_{1}(\mathbf{r}') - n_{0}(\mathbf{r}') \right), \quad (5.24)$$

where $n_1(\mathbf{r}) = n_{out}(\mathbf{r})$ and $n_0(\mathbf{r}) = n_{in}(\mathbf{r})$ for the current KS step of interest, the HXC kernel $f_{\text{HXC}}[n](\mathbf{r}, \mathbf{r}')$ is:

$$f_{\rm HXC}[n](\mathbf{r}, \mathbf{r}') = \chi_{\rm S}^{-1}[n](\mathbf{r}, \mathbf{r}') - \chi^{-1}[n](\mathbf{r}, \mathbf{r}'), \qquad (5.25)$$

and $\chi_s^{-1}[n](\mathbf{r},\mathbf{r}') = \delta v_s[n](\mathbf{r})/\delta n(\mathbf{r}') \ (\chi^{-1}[n](\mathbf{r},\mathbf{r}') = \delta v[n](\mathbf{r})/\delta n(\mathbf{r}'))$ is the non-interacting (interacting) inverse density-density response matrix. Calculating $f_{\text{HXC}}[n](\mathbf{r},\mathbf{r}')$ is quite challenging, and has recently been evaluated with time dependence for some simple systems [270].

We emphasize that $n_{out}(\mathbf{r})$ is a functional of $n_{in}(\mathbf{r})$ and does not depend on λ at all. Thus Eqs. (5.23) and (5.24) are strictly functionals of the input density $n_0(\mathbf{r})$ alone.

Towards the end of approximating the optimal λ , one may fit $E_{\nu}[n_{\lambda}]$ given some information on the derivatives. At the end points the derivatives simplify to

$$E_{\nu}'(0) \equiv \int d^3r \left(v_{s,1}(\mathbf{r}) - v_{s,0}(\mathbf{r}) \right) \left(n_1(\mathbf{r}) - n_0(\mathbf{r}) \right)$$
(5.26)

$$E'_{\nu}(1) \equiv \int d^3r \left(v_{\rm HXC}^1(\mathbf{r}) - v_{\rm HXC}^0(\mathbf{r}) \right) \left(n_1(\mathbf{r}) - n_0(\mathbf{r}) \right),$$
(5.27)

where $v_{s,j}(\mathbf{r}) = v_s[n_j](\mathbf{r})$ and $v_{HXC}^j(\mathbf{r}) = v_{HXC}[n_j](\mathbf{r})$. We find that in many systems a Hermite spline fit [252] (using $E_v(0)$, $E_v(1)$, and the derivatives $E'_v(0)$ and $E'_v(1)$) is a good approximation to the



Figure 5.8: Taking a second step in the KS scheme for a strongly correlated system (H₄ with R = 4). Panel (a) shows the input density which is near to the exact density (the $\lambda = 42\%$ density of the NI input density of Fig. 5.7) and the resulting output density, which is far from the ground-state. The lower panel (b) plots Eq. (5.22), and the inset (c) magnifies the small λ region.

energy curve $E_{\nu}(\lambda)$, or at least to where it attains the minimum. However, this fit requires an inversion to find $E_{\nu}(0)$ and $E'_{\nu}(0)$, which may be impractical for standard KS calculations.

5.5.3 Why convergence is difficult for strongly correlated systems

In this section, we discuss an important reason why convergence is difficult for strongly correlated systems, and mention some algorithms which counteract the underlying problem. Frequently, systems with strong static correlation possess a small gap [271], which in turn makes convergence difficult [256]. We can understand this difficulty by considering the non-interacting density-density response matrix $\chi_s(\mathbf{r}, \mathbf{r}')$:

$$\boldsymbol{\chi}_{\mathrm{S}}(\mathbf{r},\mathbf{r}') = 2\sum_{i\neq j}^{\infty} \frac{f_j - f_i}{\varepsilon_j - \varepsilon_i} \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}) \phi_i^*(\mathbf{r}') \phi_j(\mathbf{r}'), \qquad (5.28)$$

where $0 \le f_j \le 1$ is the Fermi occupation of orbital $\phi_j(\mathbf{r})$. For a small gap system, $\varepsilon_{LUMO} - \varepsilon_{HOMO}$ is particularly small, making that term in $\chi_s(\mathbf{r}, \mathbf{r}')$ especially large. This means that small changes in the KS potential can produce large changes in the density, which makes convergence in the KS scheme difficult. We can visualize this property by performing a singular value decomposition on $\chi_s(\mathbf{r}, \mathbf{r}')$, as in Eq. (5.16). Equivalently, since $\chi_s(\mathbf{r}, \mathbf{r}')$ is symmetric in \mathbf{r}, \mathbf{r}' , we can diagonalize $-\chi_s(\mathbf{r}, \mathbf{r}')$:

$$\chi_{\rm s}(\mathbf{r},\mathbf{r}') = -\sum_{\beta=1}^{\infty} a_{\beta} M_{\beta}(\mathbf{r}) M_{\beta}(\mathbf{r}'), \qquad (5.29)$$

where $M_{\beta}(\mathbf{r}) (a_{\beta})$ are the eigenvectors (eigenvalues) of $-\chi_{s}(\mathbf{r}, \mathbf{r}')$. Since $\chi_{s}(\mathbf{r}, \mathbf{r}')$ is negative definite, we can order $a_{\beta} \ge a_{\beta+1} > 0$. The breakdown in Eq. (5.29) physically means that a change in the KS potential along the direction $-M_{\beta}(\mathbf{r})$ produces a change in the density along $M_{\beta}(\mathbf{r})$ with a magnitude given by a_{β} , at least to first order. We therefore call $M_{\beta}(\mathbf{r})$ the density response vectors and a_{β} the response amplitudes of $\chi_{s}(\mathbf{r}, \mathbf{r}')$. The amplitudes depend on the normalization of $M_{\beta}(\mathbf{r})$, and the standard squared (L^{2}) norm is not the most natural choice. Because $M_{\beta}(\mathbf{r})$ corresponds to a change in density, we choose $\int d^{3}r |M_{\beta}(\mathbf{r})| = 2$ so that $M_{\beta}(\mathbf{r})$ can be thought of as moving an electron from one region (where $M_{\beta}(\mathbf{r}) < 0$) to another (where $M_{\beta}(\mathbf{r}) > 0$). Finally, because a_{β} are ordered by importance, $\chi_{s}(\mathbf{r}, \mathbf{r}')$ can be accurately and efficiently represented by truncating the sum once a_{β} drops below some tolerance.

We can easily find the density response vectors $M_{\beta}(x)$ for the 1d H₄ systems we have already discussed at length, which allows us to diagnose our convergence difficulties. In Fig. 5.9, we plot the first few most important $M_{\beta}(x)$. The first two ($\beta = 1, 2$) look similar for the weakly correlated and the strongly correlated systems, though the response amplitudes a_{β} are quite different. If the potential changes in the direction $-M_1(x)$, it drives a strong density response in the direction $M_1(x)$ due to the large response amplitude $a_1 = 4.75$ at R = 2 and $a_2 = 27.4$ at R = 4. Luckily, we can assume reflection symmetry, so that in the iteration of the KS equations we do not have to worry about contributions from these $\beta = 1$ terms. But now consider the symmetric $\beta = 2$ terms. If the



Figure 5.9: The most important density response functions $M_{\beta}(x)$ from Eq. (5.29) and their response amplitudes a_{β} , for the weakly correlated system (R = 2) in the top panel, and the strongly correlated system (R = 4) in the bottom panel. The locations of the atoms are shown in solid grey circles.

KS potential changes in the direction $-M_2(x)$, the density will respond by changing in the direction $M_2(x)$, and the response amplitude is very strong for the R = 4 system ($a_2 = 16.3$).

These (ground-state) response properties can be used to explain the problems that we have converging the strongly correlated H₄. If the initial KS potential puts most of the density around the central two atoms, to compensate the next trial KS potential (5.10) will increase in the central region and decrease for the edge atoms. In response, the new density will place too many electrons on the edge atoms. We have already seen this in Figures 5.6 and 5.7 with the NI starting densities. The reverse can also happen, where most of the input density is on the edge atoms, and the output density is more centralized. For the strongly correlated H₄, this "sloshing" back and forth can be particularly strong because the response amplitude a_2 is quite large – this problem plagues densities even very close to the ground state, as seen in Fig. 5.8. As $R \rightarrow \infty$, a_2 diverges, making it more and more difficult to converge. To ameliorate these problems, some convergence schemes artificially increase the gap [255] or populate otherwise unoccupied orbitals [272]. For other discussions on this matter, see Ref. [273] and for implications for time-dependent DFT, Ref.

[274].

5.5.4 Convergence as correlations grow stronger

In this section, we explore convergence within the simplest density functional approximation, the local density approximation (LDA) [39], in order to understand some basic limits on convergence as well as its dependence on the KS gap, i.e. the HOMO-LUMO gap. A simple expression for the LDA is available for our model 1d systems [33, 35]. We expect the LDA to converge in a similar way to the exact functional, especially when the KS gap of the system is close for both self-consistent LDA and exact solutions [275]. We therefore use it to study more broadly the convergence behavior of the KS scheme applied to H₂ with variable bond length. As before, changing the bond length allows us to tune the strength of the correlation: at small bond lengths the system is weakly correlated and at large bond lengths strong static correlation arises [35]. To aggravate convergence difficulties, we choose the initial density to be entirely centered on one atom [37], and determine the λ values for which the KS scheme will converge, as well as how quickly. Furthermore, we enforce spin-symmetry, so while the restricted LDA energy is wrong in the $R \rightarrow \infty$ limit [35], we expect to see convergence behavior similar to the exact functional [37].

In Fig. 5.10, we plot the number of iterations required to converge an LDA calculation to $\eta < 10^{-8}$ as a function of λ , for a variety of bond lengths R. Each curve ends at $\lambda_c(R)$, the largest λ for which the damped KS algorithm converges from this initial density. For a weakly correlated system (e.g. R = 2), a very large λ will produce convergence, and the optimal λ to converge in the fewest iterations is also fairly large (around 0.5 for R = 2). As the bond length is stretched, both the critical λ , $\lambda_c(R)$, as well as the optimal $\lambda_O(R)$ decrease. In response, the minimum number of iterations $N_{\min}(R)$ to converge to a tolerance $\eta < 10^{-8}$, increases. For example, $N_{\min}(R = 2) = 12$ for $\lambda_O(R = 2) \approx 0.5$. Considering the iterations it takes to converge as a function of λ , we see that as λ decreases past the optimal λ , it begins to take longer to converge the calculation. For $\lambda \to 0$,



Figure 5.10: The number of iterations required to converge an LDA calculation to $\eta < 10^{-8}$ (5.12), as a function of λ , for various bond-lengths *R* of the H₂ molecule, starting with an initial density of H⁻ on the left atom. The asymptotic form for small λ can be well-approximated by $7/\lambda$ for the data shown.

we approach an asymptote that appears valid for all values of *R*, given this initial starting point in the H₂ system: $N_{\text{asym}}(\lambda) = 7/\lambda$. While this is by no means a universal asymptote for all systems, we recognize there is a fundamental limit to how quickly we can converge as $\lambda \to 0$.

In Fig. 5.11, we plot the convergence-critical λ value as a function of the bond length *R*, as well as the KS gap of both the LDA and exact systems. The LDA KS gap decays at about the same rate as the critical λ , an observation that makes sense given that the KS gap has such an important role in convergence – the smaller the gap the more difficult it is to converge the calculation [275]. For bond lengths $R \leq 4$, the LDA KS gap is quite close to the exact KS gap, so that we expect similar convergence behavior for the exact functional. However, as *R* increases, the true KS gap decays more quickly than the LDA KS gap, so that the exact calculation has an even greater difficulty converging [37]. It could be that some values of λ larger than λ_c allow for convergence if the density fortuitously lands close enough to the ground state in some iteration, but there is no systematic approach to find these λ .


Figure 5.11: Plotting λ_c for an LDA calculation, as a function of the bond length *R* of a stretched hydrogen molecule, starting with the exact H⁻ density on one atom as well as KS gaps for both the LDA and exact systems.

5.5.5 Classifying convergeability

In this section, we want to mathematically investigate the the space of densities that allow convergence and how quickly that occurs. That is, given some initial density and a fixed value of λ , can we determine whether the KS scheme will converge within some given number of iterations? With λ too large, the KS scheme will be doomed to repeatedly overstep the ground-state density.

To quantify these ideas, define $\eta^{M}[n](\lambda)$ to be the value of η defined by Eq. (5.12) after *M* iterations of the KS equations with a fixed mixing of λ , starting with the input density $n(\mathbf{r})$. Then define the density set:

$$S^{M}_{\mathcal{L}}(\lambda) \equiv \left\{ n(\mathbf{r}) \text{ s.t. } \eta^{M}[n](\lambda) < \zeta \right\}.$$
(5.30)

This set describes the densities $n(\mathbf{r})$ which converge to $\eta < \zeta$ in a finite number of iterations (*M*),



Figure 5.12: The first few steps (numbered) in the KS scheme from some arbitrary starting density for H₄ with R = 4 in the LDA approximation. Numerical precision makes the energy data noisy. Metric distances are compared with the LDA ground state. Figure (a) plots the energy and (b) the metric as a function of the accumulated λ step. The density $n_{\lambda}(x)$ with the lowest metric distance is not the energetic minimum, but they are fairly close.

given a fixed- λ iteration of the KS equations. For example, $S_{\zeta}^{1} \equiv S_{\zeta}^{1}(\lambda = 1)$ is the set of input densities $n_{in}(\mathbf{r})$ that are within $\eta < \zeta$ of their output densities. (For one step, λ does not matter.) This set (5.30) allows us to quantify the different levels of convergence hell. S_{ζ}^{1} is the lowest level, and includes the ground-state density. $S_{\zeta}^{2}(1)$ is the second level, and also includes the ground-state density. $S_{\zeta}^{2}(1)$ is the second level, and also includes the ground-state density. Second level, $S_{\zeta}^{M}(1)$ reaches out to the *M*th level of hell: the set of densities which converge to within $\eta < \zeta$ within a finite number of full-KS-step iterations. All other densities belong to the $\lambda = 1$ limbo density set, densities which are doomed to wander for (essentially) all eternity, never to converge. Similarly, there are less-strict convergence sets for $\lambda < 1$, which describe a sort of density purgatory.

It might be hoped to connect these abstract convergence sets with some concrete measure, say some metric between the ground-state density and the density inputted into the KS scheme, $\eta[n, n_{g.s.}]$. Here we simply define the metric similarly to our η convergence quantifier:

$$\eta[n_1, n_2] = \int d^3r \left(n_1(\mathbf{r}) - n_2(\mathbf{r}) \right)^2 / N^2.$$
(5.31)

The idea of a metric on the set of densities is not new [276, 277]. Unfortunately, current metrics are not guaranteed to correlate e.g. a given input density $n(\mathbf{r})$ with a given convergence set $S_{\zeta}^{M}(\lambda)$. That is, there is likely no function $g_{\zeta}^{M}(\lambda)$ for which $\eta[n, n_{g.s.}] < g_{\zeta}^{M}(\lambda) \Longrightarrow n(\mathbf{r}) \in S_{\zeta}^{M}(\lambda)$. In Fig. 5.12 we show why. For λ_{+} the accumulated λ throughout the KS scheme, we see that the metric $\eta[n_{\lambda_{+}}, n_{g.s.}]$ tracks well with the how close the energy $E_{v}[n_{\lambda_{+}}]$ is to the ground state energy (at least for this example, 1d H₄ in LDA). Despite this nice relationship between the energy and the metric, a small $\eta[n, n_{g.s.}]$ does not necessarily mean we can take a large step in λ each iteration. Therefore we do not know how many steps it will take nor how small a λ is required based on the metric alone. More physically motivated metrics might remedy this issue, but we must leave this question open.

5.5.6 Spin DFT

In this section we extend the exact functional to include spin dependence. We test the exact spindependent functional on the case of stretched H_2 , starting our KS scheme with a broken-spinsymmetry solution, to determine whether or not the exact functional will find the correct spinsinglet ground state [37].

Treating the up-spin and down-spin electrons separately leads to much improved density functional approximations, as well as new challenges [278, 279]. If an unbalanced spin-state is provided as input to the KS scheme, approximate spin-density functionals may find a broken spin symmetry when the ground state should be a singlet. This is the case for many open-shell systems as bonds are stretched. The simplest such system, and a paradigm of DFT failures, is stretched H_2 [35, 96, 97, 280]. In this case, it is clear that the exact XC spin-density functional does not break symmetry at the solution density, since the ground state of any two-electron system is a singlet (in the absence of external magnetic fields) [97]. This is true of both the interacting wavefunction and the KS Slater determinant, which is then just a doubly occupied molecular orbital.



Figure 5.13: Starting an exact KS calculation of stretched H₂ with a spin-polarized density still converges to the correct spin-singlet density. Through the iterations *i*, we plot (a) the polarization density $n_{\uparrow}(x) - n_{\downarrow}(x)$ and (b) the up KS potentials $v_{s,\uparrow}(x)$; the down potentials are the mirror images.

To investigate these issues, we must first add spin-dependence to our functional, which is simple enough in principle. The added challenge is needing the ability to solve an interacting system with different potentials for spin-up and spin-down electrons, i.e. electrons in a collinear magnetic field. Similar to (5.18), the HXC potential for spin- σ electrons is:

$$v_{\text{HXC},\sigma}[n_{\uparrow},n_{\downarrow}](\mathbf{r}) = v_{\text{S}}[2n_{\sigma}](\mathbf{r}) - v_{\sigma}[n_{\uparrow},n_{\downarrow}](\mathbf{r}), \qquad (5.32)$$

where the KS potential for the up electrons can be inverted independently of the down electrons by doubly occupying the up density [281] (and vice versa for down electrons), and $v_{\sigma}[n_{\uparrow}, n_{\downarrow}](\mathbf{r})$ is the spin- σ potential necessary to produce spin densities $n_{\uparrow}(\mathbf{r})$ and $n_{\downarrow}(\mathbf{r})$ from an interacting Hamiltonian. We now investigate the use of the exact spin-dependent functional in a system where standard approximate functionals have multiple stationary points.

To test whether the exact functional can find the singlet solution for the stretched H₂ case, we start

the exact KS calculation with a spin-polarized initial density, with the up electron on the left atom and the down electron on the right. With this input, the KS scheme using the local spin-density approximation converges to a broken symmetry solution [35]. But as seen in Fig. 5.13, the exact functional finds the correct spin-singlet density without much trouble. (For this system, a large density mixing was used, namely $\lambda = 50\%$.) So long as the spin-densities are *v*-representable, the arguments of Ref. [260] apply, and there is only one stationary point of the exact functional – the true ground-state density. This is true not only in 1d (as we have illustrated) but also in 3d.

5.5.7 Non *v*-representable densities

An important question that has haunted density functional theory since the proofs of Hohenberg and Kohn is that of *v*-representability [251], i.e., for a given density $n(\mathbf{r})$, does there exist a onebody potential $v[n](\mathbf{r})$ for which it is the ground-state density? The constrained-search formulation of Levy [112] and of Lieb [219] bypasses this issue by defining the functional F[n] as an infimum over a given class of wavefunctions. But our methodology of performing both interacting and non-interacting inversions essentially requires *v*-representability in both the interacting and noninteracting systems. (In fact, $v_{\text{HXC}}[n](\mathbf{r})$ is ill-defined if $n(\mathbf{r})$ is not *v*-representable [219, 246?].) In all our calculations to date, we have had no difficulty with *v*-representability, but in the present section, we use explore its meaning in more detail.

To be clear, we consider a density *v*-representable if it is *ensemble v*-representable. The generalization to mixed states (ensembles) is important for degenerate systems, where not every density comes from a pure-state wavefunction [219, 245, 249, 282]; these practical details impact the calculations for and the values of the functionals F[n] and $T_s[n]$ [37, 219, 283], but they are not our primary concern. In addition, we focus on *non-interacting v*-representability; the challenges for interacting *v*-representability are similar, though the sets of interacting and non-interacting *v*representable densities may in principle be different. Definitive work by Chayes *et al.* [284] proves that on a grid, certain simple restrictions on the density determine the set of ensemble *v*-representable densities (in both interacting and non-interacting cases). This result explains why we were always able to find potentials for a given density on a grid in 1d, where there is no degeneracy except for spin. The work of Chayes *et al.* is reassuring, but not the final word on *v*-representability. On a grid, the kinetic energy operator (proportional to the Laplacian) is always bounded, whereas in the continuum it is not. In such cases, inverting a density for the KS potential as in Eq. (5.13) may lead to unacceptable divergences, even for reasonable densities. Proofs of *v*-representability on a grid [253] therefore do not guarantee *v*-representability in the continuum. Complicating matters, properties which make for reasonable densities and potentials differ based on the dimensionality of the problem [219]. In this section, we therefore move away from our 1d grids and instead concentrate on real 3d systems in the continuum.

In principle, one can invert any density $n(\mathbf{r})$ with $N \leq 2$ for its KS potential $v_{\rm S}[n](\mathbf{r})$, as in Eq. (5.13). Such an inversion, however, may lead to a potential which is singular and which does not have a well-defined ground state. In order to avoid these problems, the potential should satisfy two key properties: (1) the KS Hamiltonian (5.5) being bounded from below, and (2) the KS Hamiltonian being self adjoint ². Properties which make the potential reasonable translate into properties that the density should satisfy. In three dimensions, our reasonable potentials are in the set $L^{3/2} + L^{\infty}$, which describes potentials of atoms, molecules, and solids ³. The density space whose dual is $L^{3/2} + L^{\infty}$ is $L^1 \cap L^3$, and this space is a good start for the set of reasonable densities [219]. The L^p space consists of functions whose p norm is finite:

$$L^{p} \equiv \left\{ f(\mathbf{r}) : \left(\int d^{3}r |f(\mathbf{r})|^{p} \right)^{1/p} < \infty \right\},$$
(5.33)

where the integral is taken in the Lebesgue sense [?]. Thus our densities $n(\mathbf{r})$ should at least be

²Self-adjointness can be proven for certain sets of potentials. For example, if the KS potential is in the $L^2 + L^{\infty}$ space, the KS Hamiltonian is self-adjoint [?].

³One may argue that there are many reasonable 3d potentials not in $L^{3/2} + L^{\infty}$, such as the 3D isotropic harmonic oscillator: $v(\mathbf{r}) = \frac{1}{2}kr^2$. Such potentials do not describe real atoms, molecules, and solids, however, so we consider them unrealistic. For a more tolerant viewpoint and in-depth mathematical discussion, see Ref. [?].

in $L^1 \cap L^3$, and our potentials in $L^{3/2} + L^{\infty}$. (This set includes Coulomb potentials [219].) For a density whose inverted potential is *not* in $L^{3/2} + L^{\infty}$ we say this density is non-*v*-representable.

To avoid unphysical densities, one should impose non-negativity and finite kinetic energy on the density, as articulated first by Lieb [219, 246, 284]:

$$\int d^3 r \, n(\mathbf{r}) = N < \infty, \ n(\mathbf{r}) \ge 0 \ \forall \, \mathbf{r}, \quad T_{\rm S}^{\rm vW}[n] < \infty, \tag{5.34}$$

where the von Weizsäcker kinetic energy is

$$T_{\rm s}^{\rm vW}[n] \equiv \int d^3r \, \frac{|\nabla n(\mathbf{r})|^2}{8\,n(\mathbf{r})},\tag{5.35}$$

which is a lower-bound to the true kinetic energy T[n] of the system. We refer to such Lieballowed densities (which satisfy Eq. (5.34)) as reasonable. Reasonable densities comprise a subset of $L^1 \cap L^3$ (by Sobolev's inequality, Ref. [219]), so they have many useful properties. For example, for a reasonable density $n(\mathbf{r})$ in a reasonable potential $v(\mathbf{r})$ (i.e. $v(\mathbf{r})$ is in $L^{\infty} + L^{3/2}$), the potential energy $|V[n]| < \infty$ [219]. A density $n(\mathbf{r})$ which fails to satisfy Eq. (5.34) can safely be regarded as having an infinite F[n] (or $T_{\rm s}[n]$ for non-interacting systems) [219], and thus will be avoided in any iteration of the Kohn–Sham equations. Reasonable densities are not always *v*-representable, however: the inverted potential may not be in $L^{\infty} + L^{3/2}$. But in these instances, there always exists a *v*-representable density $\tilde{n}(\mathbf{r})$ that approximates the reasonable density $n(\mathbf{r})$ to any desired accuracy, and which allows the energies $F[\tilde{n}]$ and $T_{\rm s}[\tilde{n}]$ to be calculated [219, 246]. In the remainder of this section, we will explore such an example within the realm of non-interacting *v*-representability, or $v_{\rm s}$ -representability for short.

We consider a density which satisfies Eq. (5.34) but which is not v_s -representable. Inspired by the fourth example of Englisch and Englisch [244], we choose:

$$n_{\rm P}(\mathbf{r}) = A \left(1 + |r - 1|^{3/4} \right)^2 e^{-2r}, \tag{5.36}$$

where we normalize to two electrons with

$$A = \frac{256e^2}{\pi (596e^2 + 273B + 506C)}$$
(5.37)
\$\approx 0.196521 (5.38)

with

$$B = \sqrt{2\pi} \left(1 + \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{2}} dt \exp(t^2) \right)$$
 (5.39)

$$C = \frac{3}{2^{\frac{3}{4}}} \left(\Gamma \left[\frac{3}{4} \right] - \int_0^2 dt \frac{\exp(t)}{t^{\frac{1}{4}}} \right).$$
(5.40)

This pathological density $n_{\rm P}(\mathbf{r})$ is not $v_{\rm S}$ -representable due to the kink encountered at r = 1, which would require an inadmissible infinite-discontinuity in the KS potential. To see this, we attempt to invert $n_{\rm P}(\mathbf{r})$ for its KS potential via Eq. (5.13):

$$v_{\rm S}[n_{\rm P}](\mathbf{r}) \stackrel{?}{=} \frac{1}{2} - \frac{1}{r} + \frac{3}{4\left(1 + |r - 1|^{3/4}\right)} \left[-\frac{1}{8|r - 1|^{5/4}} + \frac{\delta(r - 1)}{|r - 1|^{1/4}} - \frac{\operatorname{sgn}(r - 1)}{|r - 1|^{1/4}} \left(1 - \frac{1}{r}\right) \right],$$
(5.41)

where we have used $\partial_x |x| = \operatorname{sgn}(x)$, $\partial_x^2 |x| = 2\delta(x)$, and $\operatorname{sgn}(x)$ is the sign function. The worst offender is the term proportional to $\delta(r-1)/|r-1|^{1/4}$ which fails to be in the set $L^{3/2} + L^{\infty}$. This makes $n_P(\mathbf{r})$ non- v_s -representable, since it may not even be the ground state of Eq. (5.41). Furthermore, calculating $T_s[n]$ using the second-derivative formula of Eq. (5.8) is ill-defined, due to this discontinuity. Nevertheless, $n_P(\mathbf{r})$ is reasonable: its $T_s^{VW}[n_P]$ is finite, as we will soon show. So, despite the density being reasonable, it is non- v_s -representable. And while we are focusing on non-interacting electrons, it is clear that $n_{\rm P}(\mathbf{r})$ would be troublesome for interacting electrons as well.

We obtain $T_{\rm S}^{\rm vW}[n_{\rm P}]$ by first calculating its kinetic energy density. Due to spherical symmetry, we have:

$$t_{\rm S}^{\rm vW}[n_{\rm P}](r) = \frac{1}{2} \left(\frac{d}{dr} \sqrt{n_{\rm P}(r)}\right)^2 = \frac{A}{2} \left(-1 - |r-1|^{3/4} + \frac{3\,{\rm sgn}(r-1)}{4\,|r-1|^{1/4}}\right)^2 e^{-2r},\qquad(5.42)$$

so that

$$T_{\rm S}^{\rm vW}[n_{\rm P}] = 4\pi \int_0^\infty dr \, r^2 t_{\rm S}^{\rm vW}[n_{\rm P}](r) = \frac{A\pi}{128e^2} \left(40e^2 + 93B - 13C\right)$$
(5.43)

$$\approx 0.996519. \tag{5.44}$$

Calculating $T_{\rm S}[n_{\rm P}]$ via the second-derivative formula (5.8) seems like a simple integration by parts:

$$T_{\rm s}[n] = -\frac{1}{2} \int d^3 r \sqrt{n(\mathbf{r})} \nabla^2 \sqrt{n(\mathbf{r})} \\ = -\int d^3 r n(\mathbf{r}) v_{\rm s}[n](\mathbf{r})$$

$$(N \le 2), \qquad (5.45)$$

but due to the discontinuities in $v_{\rm S}[n_{\rm P}](\mathbf{r})$ (5.41), this integral is ill-defined for $n_{\rm P}(\mathbf{r})$.

We now illustrate how to obtain a v_s -representable density that is arbitrarily close to our reasonable density $n_P(\mathbf{r})$. As a bonus, this procedure will also give a well-defined kinetic energy using the second-derivative formula. Consider a function $f_{\gamma}(x)$ that smooths out the |r-1| in Eq. (5.36), but which has a parameter which can be continuously adjusted so that $\lim_{\gamma \to 0} f_{\gamma}(r-1) = |r-1|$. We



Figure 5.14: Inverting $n_{\gamma}(r)$ of Eq. (5.47) for the KS potential. As γ becomes smaller and smaller, the changes in potential near r = 1 become larger and larger.

choose

$$f_{\gamma}(x) = \sqrt{x^2 + \gamma^2},\tag{5.46}$$

setting

$$n_{\gamma}(\mathbf{r}) = A_{\gamma} \left(1 + f_{\gamma}^{3/4}(r-1) \right)^2 e^{-2r}.$$
(5.47)

(Note that the density must be renormalized for each value of γ .) For small γ , the metric distance between $n_{\rm P}(\mathbf{r})$ and $n_{\gamma}(\mathbf{r})$, $\eta [n_{\rm P}, n_{\gamma}]$ (5.31), is proportional to $\gamma^{2.5}$; and $n_{\gamma}(\mathbf{r})$ remains *v*-representable for all $\gamma > 0$. In the iterations of the Kohn–Sham scheme, tolerances between densities are already built into the method—namely as in Eq. (5.12)—so we need no greater accuracy than that when finding a *v*-representable density close enough to the target density.

As already mentioned, even though $T_{\rm S}^{\rm vW}[n_{\rm P}]$ is finite, $T_{\rm S}[n_{\rm P}]$ via Eq. (5.45) is ill-defined. But by using the smoothed density of Eq. (5.47), we can calculate $T_{\rm S}[n_{\gamma}]$ and take the limit $\gamma \rightarrow 0$ (see Fig. 5.15). The result is the the same as $T_{\rm S}^{\rm vW}[n_{\rm P}]$, and this must be so based on simple mathematical



Figure 5.15: Kinetic energy convergence of $n_P(r)$ from Eq. (5.47) by smoothing out the kink as in Eq. (5.36). While the von Weizsäcker kinetic energy (vW) may be evaluated and integrated using only one derivative of the density, higher order derivatives of the density develop nonintegrable features.

considerations [284]. Two conjectures might be made after consider the foregoing:

- 1. A density being *v*-representable requires some bounds on the Laplacian (or second derivative) of the density. On a grid, this is not an issue because the Laplacian is always bounded.
- 2. Finite energies F[n] and $T_{\rm S}[n]$ may be extracted from reasonable but non-v-representable densities. This can be done by suitably smoothing (or discretizing) the density and carefully taking limits, so as to remove divergent terms. For $N \leq 2$, $T_{\rm S}^{\rm vW}[n]$ should give the limit of $T_{\rm S}[n]$ properly, and for N > 2 one should be able to use

$$T_{\rm s}[n] = \sum_{j=1}^{N/2} \int d^3 r \, |\nabla \phi_j(\mathbf{r})|^2, \tag{5.48}$$

to avoid any singular divergences from second derivatives.

For some concluding remarks, recall that the exact $E_{\text{HXC}}[n]$ is defined using both interacting and non-interacting systems. This means that we need $n(\mathbf{r})$ to be v_{s} and *v*-representable to calculate

 $E_{\text{HXC}}[n]$. While in principle v_{S} -representable densities comprise a different set than *v*-representable densities, we can use the methods of this section to calculate $E_{\text{HXC}}[n]$ for any reasonable density. The prescription is to find a v_{S} -representable density $\tilde{n}_{\text{S}}(\mathbf{r})$ and a *v*-representable density $\tilde{n}(\mathbf{r})$ which are within some small tolerance of $n(\mathbf{r})$ and each other. With the inverted potentials $\tilde{v}_{\text{S}}(\mathbf{r})$ and $\tilde{v}(\mathbf{r})$, self-consistent KS calculations are possible, given $v_{\text{HXC}}[n](\mathbf{r}) = \tilde{v}_{\text{S}}(\mathbf{r}) - \tilde{v}(\mathbf{r})$ as in Eq. (5.18). We hope to further explore the connections between interacting and non-interacting *v*-representability in future work.

As a final note, all of our numerical inversions have used pure-state wavefunctions. This is justified for spin-singlet 1d systems and for this simple spin-singlet example in 3d. In systems with degeneracy, however, the ensemble formulation of DFT should be used, not only because the ensemble $E_v[n]$ is convex [37], but also because the class of pure-state *v*-representable densities is smaller than the class of ensemble *v*-representable densities [219, 246, 249]. Outside of this section, we always worked on a grid, which means that *v*-representability difficulties were not an issue [284]. We found no cases where, as the grid spacing goes to zero, the potential diverged as in the example here.

5.6 Conclusions

Our investigations into the exact functional demonstrate that it is possible to solve the Kohn–Sham equations with the exact XC functional for simple model systems at great computational cost. Our calculations involve mapping the functional landscape for more than just the ground-state density, enabling us to address questions of convergence within the KS scheme. We tested many systems, and found that strongly correlated systems pose a greater challenge, not only from a theoretical standpoint in finding accurate approximations, but also practically within the KS scheme, where smaller steps must be taken (or more sophisticated methods used) to converge the calculation. In a word, the exact functional landscape for strongly correlated systems is more treacherous, but not

impossible, for a simple KS algorithm to navigate.

Despite the surmountable convergence difficulties for strongly correlated systems, the only stationary point of the KS equations is the ground-state density of the original problem, given *v*representable densities as inputs. This is simply a reaffirmation of the HK theorem, that there is a one-to-one correspondence between ground state densities and potentials. This is the case even for stretched systems, where approximate functionals would prefer to break spin symmetry; the exact spin-density functional has only one stationary point, at the correct ground-state spin densities. All changes in density away from that point cause the energy to rise. Thus the lowest energy stationary point with an approximate functional has the same energy landscape as the true functional, and should be treated as the prediction for the energy with that approximation, regardless of how many symmetries have been broken. This reaffirms the conclusions of Ref. [97].

The density mixing algorithm used to prove convergence of the KS scheme is one of the simplest ways to explore the infinite-dimensional set of possible densities, and it provides insight into the gradient-descent nature of the KS scheme. While this algorithm is too primitive for modern practical implementations, its main purpose here is to provide a definite framework in which convergence questions can be studied.

There is another avenue of research, but which cannot be pursued in these model 1d systems: the effects of orbital degeneracy within exact KS theory, especially due to angular momentum. An ensemble of degenerate densities may easily not be pure-state *v*-representable [219, 246], and the extent of the challenges for exact DFT warrants investigation. Unfortunately, this avenue cannot be explored for these 1d systems, in which there is no angular momentum. Exploring these concepts in 3d would shed light on how DFT handles strong correlation effects due to *exact* degeneracies, in contrast to the near degeneracies [285] we have investigated (e.g. in stretched H₂) for which exact DFT performs well in 1d [37].

Finally, we discuss the consequences of our example of a non v-representable density. The example

we give is a reasonable density, meaning it is in the domain on with the Levy–Lieb density functional is defined: it is normalized, non-negative, and has finite kinetic energy. Consistent with the proof of Chayes et. al. [284], on any finite grid, it has a well-behaved Kohn–Sham potential. But as the grid-spacing is brought to zero, divergences appear in that potential, so that it is ill-defined in the continuum limit. So this is an example of a density that is *v*-representable on a lattice, but is not *v*-representable in the continuum. Similarly, one can remain in the continuum and introduce a small parameter (γ) which rounds off the cusp in the density. For any finite value of γ , no matter how small, the potential is finite and well-behaved. Thus our cuspy density is arbitrarily close to a *v*-representable density. These are the standard arguments given in the physics literature for why *v*-representability is not an issue in DFT.

But our example shows that there is still something to worry about. Either regularization procedure (finite grid spacing or finite γ) fails in the limit, and anyone doing an inversion on such a density should check their KS potential converges to a well-defined limit. Our example density fails this test.

The important question is not whether some artificially created density is *v*-representable or not. The real question is, given the densities of atoms, molecules, and solids, i.e., densities generated by solving the Schrödinger equation with Coulomb interactions, are there features like that of our example that produce ill-behaved KS potentials? This is all that matters, and practical experience suggests that such situations are rare, if they occur at all.

Chapter 6

Conclusion

A theoretical program has been developed to investigate the behaviors of the exact functional. This was accomplished by using the density matrix renormalization group and a one dimensional Hubbard model, whose interaction is related to the spherically averaged Coulomb interaction. The one dimensional system was shown to reproduce the same qualitative behaviors as in real chemical systems and benchmarked. The one dimensional system was used to find exact results in density functional theory, such as exact Kohn-Sham potentials. Exact data was then used to machine learn the exact functional with kernel ridge regression and implement a self-consistent solver to use the exact functional. This was completely orbital free and obtained answers to chemical accuracy, showing that machine learning methods are sufficient to learn the functional. A study of the convergence of the exact functional was undertaken with the one dimensional system including searches for non-*v*-representable systems, none of which were found. The final chapter used a class of transformations called wavelets to renormalize a system represented on a fine lattice to a coarsened basis set. The basis set was shown to reproduce the answer on the fine lattice to chemical accuracy with 2-3 functions per electron.

Together, this comprises a complete deduction of the properties and ability to compute with the

exact functional, albeit only demonstrating this in one dimension. We have provided a thorough understanding of how such a computation would converge, the methods to construct the exact functional with machine learning methods that is orbital free and available for self-consistent computation, and an optimized basis to represent the function with as few degrees of freedom as possible.

Bibliography

- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [2] N. Schuch and F. Verstraete, Nature Physics 5, 732 (2009).
- [3] T. S. Cubitt, D. Perez-Garcia, and M. M. Wolf, Nature 528, 207 (2015).
- [4] T. E. Baker, E. M. Stoudenmire, L. O. Wagner, K. Burke, and S. R. White, Physical Review B **91**, 235141 (2015).
- [5] L. Schiff and H. Snyder, Physical Review 55, 59 (1939).
- [6] R. Elliott and R. Loudon, Journal of Physics and Chemistry of Solids 15, 196 (1960).
- [7] W. Knorr and R. Godby, Physical review letters 68, 639 (1992).
- [8] W. Knorr and R. Godby, Physical Review B 50, 1779 (1994).
- [9] L. Shulenburger, M. Casula, G. Senatore, and R. M. Martin, Physical Review B 78, 165303 (2008).
- [10] L. Shulenburger, M. Casula, G. Senatore, and R. M. Martin, Journal of Physics A: Mathematical and Theoretical 42, 214021 (2009).
- [11] M. Casula, S. Sorella, and G. Senatore, Physical Review B 74, 245427 (2006).
- [12] J. H. Eberly, Q. Su, and J. Javanainen, JOSA B 6, 1289 (1989).
- [13] C. Law, Q. Su, and J. Eberly, Physical Review A 44, 7844 (1991).
- [14] C. J. Joachain, N. J. Kylstra, and R. M. Potvliege, *Atoms in intense laser fields* (Cambridge University Press, 2012).
- [15] T. Kreibich, M. Lein, V. Engel, and E. Gross, Physical review letters 87, 103901 (2001).
- [16] M. Lein, E. Gross, and V. Engel, Journal of Physics B: Atomic, Molecular and Optical Physics **33**, 433 (2000).
- [17] S. Chelkowski, A. Conjusteau, T. Zuo, and A. D. Bandrauk, Physical Review A 54, 3235 (1996).

- [18] S. Chakravorty and E. Clementi, Phys. Rev. A **39**, 2290 (1989).
- [19] A. D. Bandrauk, *Molecules in laser fields* (CRC Press, 1993).
- [20] A. D. Bandrauk and S. C. Wallace, *Coherence phenomena in atoms and molecules in laser fields*, Vol. 287 (Plenum Publishing Corporation, 1992).
- [21] H. N. Núñez Yépez, A. L. Salas-Brito, and D. A. Solis, Phys. Rev. A 83, 064101 (2011).
- [22] D. H. Gebremedhin and C. A. Weatherford, Physical Review E 89, 053319 (2014).
- [23] M. A. Carrillo-Bernal, H. N. Núñez Yépez, A. L. Salas-Brito, and D. A. Solis, Phys. Rev. E 91, 027301 (2015).
- [24] P. M. W. G. B. G. Johnson and J. A. Pople, J. Chem. Phys. 98, 5612 (1993).
- [25] P. M. W. G. B. G. Johnson and J. A. Pople, Chem. Phys. Lett. 220, 377 (1994).
- [26] P. M. W. G. B. G. Johnson, C. A. Gonzales and J. A. Pople, Chem. Phys. Lett. 221, 100 (1994).
- [27] C. J. Umrigar and X. Gonze, Phys. Rev. A 50, 3827 (1994).
- [28] K. Capelle, N. Lima, M. Silva, and L. Oliveira, in *The Fundamentals of Electron Density*, *Density Matrix and Density Functional Theory in Atoms, Molecules and the Solid State* (Springer, 2003) pp. 145–168.
- [29] R. Magyar and K. Burke, Phys. Rev. A 70, 032508 (2004).
- [30] K. Capelle, M. Borgh, K. Kärkkäinen, and S. Reimann, Physical review letters 99, 010402 (2007).
- [31] D. Vieira, H. J. Freire, V. Campo Jr, and K. Capelle, Journal of Magnetism and Magnetic Materials 320, e418 (2008).
- [32] P.-F. Loos and P. M. W. Gill, Phys. Rev. Lett. 103, 123008 (2009).
- [33] N. Helbig, J. I. Fuks, M. Casula, M. J. Verstraete, M. A. Marques, I. Tokatly, and A. Rubio, Physical Review A 83, 032503 (2011).
- [34] K. Burke and L. O. Wagner, International Journal of Quantum Chemistry 113, 96 (2013).
- [35] L. O. Wagner, E. Stoudenmire, K. Burke, and S. R. White, Phys. Chem. Chem. Phys. 14, 8581 (2012).
- [36] E. M. Stoudenmire, L. O. Wagner, S. R. White, and K. Burke, Phys. Rev. Lett. 109, 056402 (2012).
- [37] L. O. Wagner, E. M. Stoudenmire, K. Burke, and S. R. White, Phys. Rev. Lett. 111, 093003 (2013).

- [38] L. O. Wagner, T. E. Baker, E. Stoudenmire, K. Burke, and S. R. White, Phys. Rev. B **90**, 045109 (2014).
- [39] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
- [40] K. Burke, J. Chem. Phys. **136** (2012).
- [41] K. Burke and L. O. Wagner, Int. J. Quant. Chem. 113, 96 (2013).
- [42] S. R. White, Phys. Rev. Lett. 69, 2863 (1992).
- [43] J. A. Snyman, *Practical Mathematical Optimization* (Springer, New York, 2005).
- [44] E. M. Stoudenmire and S. R. White, Annual Review of Condensed Matter Physics **111** (2012).
- [45] I. P. McCulloch, Journal of Statistical Mechanics: Theory and Experiment 2007, P10014 (2007).
- [46] U. Schollwöck, Annals of Physics 326, 96 (2011), january 2011 Special Issue.
- [47] G. M. Crosswhite, A. C. Doherty, and G. Vidal, Phys. Rev. B 78, 035116 (2008).
- [48] J. Luttinger, Journal of Mathematical Physics 4, 1154 (1963).
- [49] F. Haldane, Physical Review Letters 47, 1840 (1981).
- [50] F. D. M. Haldane, Physics Letters A 93, 464 (1983).
- [51] P. Hohenberg, Physical Review 158, 383 (1967).
- [52] C. Hwang, S. Shin, and J. Chung, in *Journal of Physics: Conference Series*, Vol. 61 (IOP Publishing, 2007) p. 454.
- [53] A. Gold and A. Ghazali, Physical Review B **41**, 7626 (1990).
- [54] S. Giraud and R. Combescot, Physical Review A 79, 043615 (2009).
- [55] S. A. Kivelson, E. Fradkin, and V. J. Emery, Nature 393, 550 (1998).
- [56] B. Tanatar, Physics Letters A 239, 300 (1998).
- [57] H. Schulz, Phys. Rev. Lett. 64, 2831 (1990).
- [58] H. Schulz, Physical review letters **71**, 1864 (1993).
- [59] S. Artemenko, G. Xianlong, and W. Wonneberger, Journal of Physics B: Atomic, Molecular and Optical Physics 37, S49 (2004).
- [60] R. Egger and H. Grabert, Physical review letters 75, 3505 (1995).
- [61] N. Lima, M. Silva, L. Oliveira, and K. Capelle, Physical review letters 90, 146402 (2003).

- [62] M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions: With Formulas, Graphs, and Mathematical Tables*, Applied mathematics series (Dover Publications, 1965).
- [63] R. Loudon, American Journal of Physics 27, 649 (1959).
- [64] B. Simon, *Infinitude or finiteness of the number of bound states of an N-body quantum system. I.*, Tech. Rep. (Princeton Univ., NJ, 1970).
- [65] B. Pirvu, V. Murg, J. I. Cirac, and F. Verstraete, New Journal of Physics 12, 025012 (2010).
- [66] L. H. Thomas, Math. Proc. Camb. Phil. Soc. 23, 542 (1927).
- [67] E. Fermi, Zeitschrift für Physik A Hadrons and Nuclei 48, 73 (1928).
- [68] E. H. Lieb and B. Simon, Advances in Mathematics 23, 22 (1977).
- [69] P. Elliot, A. Cangi, S. Pittalis, E. Gross, and K. Burke, submitted and ArXiv:1408.2434 (2014).
- [70] R. Armiento and A. Mattsson, Phys. Rev. B 72, 085108 (2005).
- [71] G. F. Giuliani and G. Vignale, eds., *Quantum Theory of the Electron Liquid* (Cambridge University Press, 2008).
- [72] J. P. Perdew and S. Kurth, "Density functionals for non-relativistic Coulomb systems in the new century," in *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. A. L. Marques (Springer, Berlin / Heidelberg, 2003) pp. 1–55.
- [73] P. N. e.g. and D. Pines, Phys. Rev. 111, 442 (1958).
- [74] M. Gell-Mann and K. Brueckner, Phys. Rev. 106, 364 (1957).
- [75] Q. Li, S. D. Sarma, and R. Joynt, Physical Review B 45, 13713 (1992).
- [76] S. D. Sarma and E. Hwang, Physical Review B 54, 1936 (1996).
- [77] Q. Li and S. D. Sarma, Physical Review B 43, 11768 (1991).
- [78] A. L. Fetter and J. D. Walecka, Quantum theory of many-particle systems, by Fetter, Alexander L.; Walecka, John Dirk. San Francisco, McGraw-Hill [c1971]. International series in pure and applied physics (McGraw-Hill, New York, NY, 1971).
- [79] G. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid*, Masters Series in Physics and Astronomy (Cambridge University Press, 2005).
- [80] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge university press, 1972).
- [81] D. C. Langreth and J. P. Perdew, Physical Review B 15, 2884 (1977).
- [82] A. Rajagopal and J. C. Kimball, Physical Review B 15, 2819 (1977).
- [83] E. Wigner, Phys. Rev. 40, 749 (1932).

- [84] J. P. M. Seidl and M. Levy, Physical Review A 59, 51 (1999).
- [85] M. Seidl, P. Gori-Giorgi, and A. Savin, Physical Review A 75, 042511 (2007).
- [86] M. Seidl, J. P. Perdew, and S. Kurth, Phys. Rev. A 62, 012502 (2000), *ibid.* 72, 029904(E) (2005).
- [87] E. D. F. P. S.J. Chakravorty, S.R. Gwaltney and C. F. Fischer, Phys. Rev. A 47, 3649 (1993).
- [88] I. Levine, Quantum Chemistry, 6th ed. (Prentice Hall, Englewood Cliffs, 2008).
- [89] K. Burke, "The ABC of DFT," (2007), available online.
- [90] M. Petersilka and E. Gross, International journal of quantum chemistry 60, 1393 (1996).
- [91] K. Burke, Lect. Notes Phys 706, 181 (2006).
- [92] C.-O. Almbladh and U. Von Barth, Physical Review B **31**, 3231 (1985).
- [93] T. Koopmans, Physica 1, 104 (1934).
- [94] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science 321, 792 (2008).
- [95] G. K.-L. Chan and M. Head-Gordon, The Journal of chemical physics 116, 4462 (2002).
- [96] C. Coulson and I. Fischer, Philosophical Magazine Series 7 40, 386 (1949).
- [97] J. P. Perdew, A. Savin, and K. Burke, Phys. Rev. A 51, 4531 (1995).
- [Burke and friends] K. Burke and friends, "The abc of dft," In preparation.
- [98] A. Pribram-Jones, D. Gross, and K. Burke, Annual review of physical chemistry **66**, 283 (2015).
- [99] A. Liechtenstein, V. Anisimov, and J. Zaanen, Physical Review B 52, R5467 (1995).
- [100] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
- [101] R. Iftimie, P. Minary, and M. E. Tuckerman, Proceedings of the National Academy of Sciences of the United States of America **102**, 6654 (2005).
- [102] E. Fermi, Rend. Acc. Naz. Lincei 6 (1927).
- [103] F. Tran and T. Wesolowski, Chem. Phys. Lett. 360, 209 (2002).
- [104] J. C. Snyder, M. Rupp, K. Hansen, K.-R. Mueller, and K. Burke, Phys. Rev. Lett. **108**, 253002 (2012).
- [105] J. C. Snyder, M. Rupp, K. Hansen, L. Blooston, K.-R. Müller, and K. Burke, The Journal of Chemical Physics 139, 224104 (2013).

- [106] L. Li, J. C. Snyder, I. M. Pelaschier, J. Huang, U.-N. Niranjan, P. Duncan, M. Rupp, K.-R. Müller, and K. Burke, submitted and arXiv:1404.1333 (2014).
- [107] K. Vu, J. C. Snyder, L. Li, M. Rupp, B. F. Chen, T. Khelif, K.-R. Müller, and K. Burke, International Journal of Quantum Chemistry **115**, 1115 (2015).
- [108] F. Sols, Phys. Rev. Lett. 67, 2874 (1991).
- [109] H. R. Sadeghpour, J. Phys. B: At. Mol. Opt. Phys. 25, L29 (1992).
- [110] U. Schollwöck, Reviews of modern physics 77, 259 (2005).
- [111] U. Schollwöck, Annals of Physics **326**, 96 (2011).
- [112] M. Levy, Proceedings of the National Academy of Sciences of the United States of America 76, 6062 (1979).
- [113] P. Mori-Sánchez, A. J. Cohen, and W. Yang, Physical review letters 100, 146401 (2008).
- [114] J. Erhard, P. Bleiziffer, and A. Görling, Physical Review Letters 117, 143002 (2016).
- [115] T. Zhu, P. de Silva, H. van Aggelen, and T. Van Voorhis, Physical Review B **93**, 201108 (2016).
- [116] J. Yang, W. Hu, D. Usvyat, D. Matthews, M. Schuetz, and G. K.-L. Chan, Science 345, 640 (2014).
- [117] O. M. Parkhi, A. Vedaldi, C. V. Jawahar, and A. Zisserman, in *IEEE International Conference on Computer Vision* (2011).
- [118] X. Zhao, J. Luan, and M. Wolff, in 2016 APWG Symposium on Electronic Crime Research (eCrime) (2016) pp. 1–5.
- [119] D. Silver, A. Huang, C. J. Maddison, A. Guez, L. Sifre, G. Van Den Driessche, J. Schrittwieser, I. Antonoglou, V. Panneershelvam, M. Lanctot, *et al.*, Nature **529**, 484 (2016).
- [120] M. Rupp, A. Tkatchenko, K.-R. Müller, and O. A. von Lilienfeld, Phys. Rev. Lett. 108, 058301 (2012).
- [121] M. Rupp, International Journal of Quantum Chemistry 115, 1003 (2015).
- [122] T. Hastie, R. Tibshirani, J. Friedman, and J. Franklin, The Mathematical Intelligencer **27**, 83 (2005).
- [123] J. C. Snyder, M. Rupp, K.-R. Müller, and K. Burke, International Journal of Quantum Chemistry 115, 1102 (2015).
- [124] M.-C. Kim, E. Sim, and K. Burke, Phys. Rev. Lett. 111, 073003 (2013).
- [125] F. Hirshfeld, Theoretica chimica acta 44, 129 (1977).

- [126] I. P. McCulloch, arXiv preprint arXiv:0804.2509 (2008).
- [127] S. R. White and R. L. Martin, The Journal of chemical physics 110, 4127 (1999).
- [128] G. K.-L. Chan and M. Head-Gordon, The Journal of chemical physics 116, 4462 (2002).
- [129] F. Brockherde, L. Li, K. Burke, and K.-R. Müller, arXiv preprint arXiv:1609.02815 (2016).
- [130] A. Pribram-Jones, D. A. Gross, and K. Burke, Annual Review of Physical Chemistry (2014).
- [131] C. D. Sherrill and H. F. Schaefer, Advances in quantum chemistry 34, 143 (1999).
- [132] C. J. Cramer, *Essentials of computational chemistry: theories and models* (John Wiley & Sons, 2013).
- [133] F. Coester and H. Kümmel, Nuclear Physics 17, 477 (1960).
- [134] J. Cizek and J. Paldus, Physica Scripta 21, 251 (1980).
- [135] J. Čížek, The Journal of Chemical Physics 45, 4256 (1966).
- [136] S. R. White, Phys. Rev. B 48, 10345 (1993).
- [137] G. K.-L. Chan and M. Head-Gordon, The Journal of chemical physics 116, 4462 (2002).
- [138] P.-O. Löwdin and H. Shull, Physical Review 101, 1730 (1956).
- [139] P.-O. Löwdin, Physical Review **97**, 1474 (1955).
- [140] H. J. A. Jensen, P. Jørgensen, H. Ågren, and J. Olsen, The Journal of chemical physics 88, 3834 (1988).
- [141] J. Eisert, M. Cramer, and M. B. Plenio, Reviews of Modern Physics 82, 277 (2010).
- [142] A. Haar, Mathematische Annalen 69, 331 (1910).
- [143] D. Gabor, Electrical Engineers-Part III: Radio and Communication Engineering, Journal of the Institution of 93, 429 (1946).
- [144] A. Grossmann and J. Morlet, SIAM journal on mathematical analysis 15, 723 (1984).
- [145] Y. Meyer, in *Wavelets* (Springer, 1989) pp. 21–37.
- [146] S. G. Mallat, IEEE transactions on pattern analysis and machine intelligence 11, 674 (1989).
- [147] I. Daubechies et al., Ten lectures on wavelets, Vol. 61 (SIAM, 1992).
- [148] I. Daubechies, Communications on pure and applied mathematics 41, 909 (1988).
- [149] I. Daubechies, SIAM Journal on Mathematical Analysis 24, 499 (1993).
- [150] S. Wei and M. Chou, Physical review letters 76, 2650 (1996).

- [151] C. Tymczak and X.-Q. Wang, Physical Review Letters 78, 3654 (1997).
- [152] R. J. Harrison, G. I. Fann, T. Yanai, Z. Gan, and G. Beylkin, The Journal of chemical physics 121, 11587 (2004).
- [153] G. Fann, R. Harrison, and G. Beylkin, in *Journal of Physics: Conference Series*, Vol. 16 (IOP Publishing, 2005) p. 461.
- [154] R. J. Harrison, G. I. Fann, Z. Gan, T. Yanai, S. Sugiki, A. Beste, and G. Beylkin, in *Journal of Physics: Conference Series*, Vol. 16 (IOP Publishing, 2005) p. 243.
- [155] G. Fann, R. Harrison, G. Beylkin, J. Jia, R. Hartman-Baker, W. Shelton, and S. Sugiki, in *Journal of Physics: Conference Series*, Vol. 78 (IOP Publishing, 2007) p. 012018.
- [156] W. S. Thornton, N. Vence, and R. Harrison, Proceedings of the Cray Users Group (2009).
- [157] R. J. Harrison, G. Beylkin, F. A. Bischoff, J. A. Calvin, G. I. Fann, J. Fosso-Tande, D. Galindo, J. R. Hammond, R. Hartman-Baker, J. C. Hill, *et al.*, SIAM Journal on Scientific Computing **38**, S123 (2016).
- [158] J. Van den Berg, *Wavelets in physics* (Cambridge University Press, 2004).
- [159] B. Natarajan, M. E. Casida, L. Genovese, and T. Deutsch, arXiv preprint arXiv:1110.4853 (2011).
- [160] T. Shiozaki and S. Hirata, Phys. Rev. A 76, 040503 (2007).
- [161] J. R. Flores, The Journal of chemical physics **98**, 5642 (1993).
- [162] H.-J. Flad, W. Hackbusch, D. Kolb, and R. Schneider, The Journal of chemical physics 116, 9641 (2002).
- [163] F. A. Bischoff, R. J. Harrison, and E. F. Valeev, The Journal of chemical physics 137, 104103 (2012).
- [164] F. A. Bischoff and E. F. Valeev, The Journal of chemical physics 139, 114106 (2013).
- [165] G. Beylkin, M. J. Mohlenkamp, and F. Pérez, Journal of Mathematical Physics 49, 032107 (2008).
- [166] L. Genovese, B. Videau, M. Ospici, T. Deutsch, S. Goedecker, and J.-F. Mehaut, Comptes Rendus Mecanique 339, 149 (2011).
- [167] T. A. Arias, Reviews of Modern Physics **71**, 267 (1999).
- [168] B. N. Khoromskij, V. Khoromskaia, and H.-J. Flad, SIAM journal on scientific computing 33, 45 (2011).
- [169] S. Nagy and J. Pipek, Physical Chemistry Chemical Physics 17, 31558 (2015).
- [170] J. Fosso-Tande and R. J. Harrison, Chemical Physics Letters 561, 179 (2013).

- [171] G. Beylkin and T. Haut, in *Proc. R. Soc. A*, Vol. 469 (The Royal Society, 2013) p. 20130231.
- [172] A. Maloney, J. L. Kinsey, and B. R. Johnson, The Journal of chemical physics 117, 3548 (2002).
- [173] G. Beylkin, N. Coult, and M. J. Mohlenkamp, Journal of Computational Physics 152, 32 (1999).
- [174] A. M. Niklasson, C. Tymczak, and H. Röder, Physical Review B 66, 155120 (2002).
- [175] S. Goedecker and O. Ivanov, Physical Review B **59**, 7270 (1999).
- [176] M. Bachmayr, Adaptive low-rank wavelet methods and applications to two-electron Schrödinger equations, Ph.D. thesis, Hochschulbibliothek der Rheinisch-Westfälischen Technischen Hochschule Aachen (2012).
- [177] T. Yanai, G. I. Fann, G. Beylkin, and R. J. Harrison, Physical Chemistry Chemical Physics 17, 31405 (2015).
- [178] G. Evenbly and S. R. White, Physical review letters 116, 140403 (2016).
- [179] G. Evenbly and S. R. White, arXiv preprint arXiv:1605.07312 (2016).
- [180] M. T. Fishman and S. R. White, Physical Review B 92, 075132 (2015).
- [181] F. Keinert, Wavelets and multiwavelets (CRC Press, 2003).
- [182] B. K. Alpert, SIAM journal on Mathematical Analysis 24, 246 (1993).
- [183] C. K. Chui and J.-a. Lian, Applied Numerical Mathematics 20, 273 (1996).
- [184] B. R. Johnson, J. L. Mackey, and J. L. Kinsey, Journal of Computational Physics 168, 356 (2001).
- [185] B. Alpert, G. Beylkin, D. Gines, and L. Vozovoi, Journal of Computational Physics **182**, 149 (2002).
- [186] F. A. Bischoff and E. F. Valeev, The Journal of chemical physics 134, 104104 (2011).
- [187] S. Raimes, (1972).
- [188] T. Helgaker, P. Jorgensen, and J. Olsen, *Molecular electronic-structure theory* (John Wiley & Sons, 2014).
- [ITe] "Calculations were performed using the itensor library: http://itensor.org/," .
- [189] G. K.-L. Chan, The Journal of chemical physics 120, 3172 (2004).
- [190] D. Ghosh, J. Hachmann, T. Yanai, and G. K.-L. Chan, The Journal of chemical physics **128**, 144117 (2008).
- [191] S. Sharma and G. K.-L. Chan, The Journal of chemical physics 136, 124121 (2012).

- [192] R. Olivares-Amaya, W. Hu, N. Nakatani, S. Sharma, J. Yang, and G. K.-L. Chan, The Journal of chemical physics **142**, 034102 (2015).
- [193] R. Bellman, Princeton, USA: Princeton University Press 1, 3 (1957).
- [194] G. Beylkin and M. J. Mohlenkamp, Proceedings of the National Academy of Sciences **99**, 10246 (2002).
- [195] J. Rust, Econometrica: Journal of the Econometric Society, 487 (1997).
- [196] W. B. Powell, *Approximate Dynamic Programming: Solving the curses of dimensionality*, Vol. 703 (John Wiley & Sons, 2007).
- [197] M. J. Reynolds, G. Beylkin, and A. Doostan, arXiv preprint arXiv:1605.05789 (2016).
- [198] L. Grasedyck, D. Kressner, and C. Tobler, GAMM-Mitteilungen 36, 53 (2013).
- [199] J. Anderson, (2010).
- [200] W. J. Glover, R. E. Larsen, and B. J. Schwartz, The Journal of chemical physics **132**, 144101 (2010).
- [201] M. P. Nightingale and C. J. Umrigar, *Quantum Monte Carlo methods in physics and chemistry*, 525 (Springer Science & Business Media, 1998).
- [202] C. Umrigar, K. Wilson, and J. Wilkins, Physical Review Letters 60, 1719 (1988).
- [203] L. Frediani and D. Sundholm, Physical Chemistry Chemical Physics 17, 31357 (2015).
- [204] S. Losilla and D. Sundholm, The Journal of chemical physics 136, 214104 (2012).
- [205] S. A. Losilla Fernández et al., (2013).
- [206] C. D. Sherrill, The Journal of chemical physics 132, 110902 (2010).
- [207] S. Wold, K. Esbensen, and P. Geladi, Chemometrics and intelligent laboratory systems 2, 37 (1987).
- [208] H. Abdi and L. J. Williams, Wiley interdisciplinary reviews: computational statistics **2**, 433 (2010).
- [209] K. Vu, J. C. Snyder, L. Li, M. Rupp, B. F. Chen, T. Khelif, K.-R. Müller, and K. Burke, International Journal of Quantum Chemistry **115**, 1115 (2015).
- [210] L. Li, J. C. Snyder, I. M. Pelaschier, J. Huang, U.-N. Niranjan, P. Duncan, M. Rupp, K.-R. Müller, and K. Burke, International Journal of Quantum Chemistry 116, 819 (2016).
- [211] L. Li, T. E. Baker, S. R. White, K. Burke, et al., Physical Review B 94, 245129 (2016).
- [212] C. A. Coulson and I. Fischer, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science **40**, 386 (1949).

- [213] F. Neese and E. F. Valeev, Journal of chemical theory and computation 7, 33 (2010).
- [214] A. Grüneis, G. H. Booth, M. Marsman, J. Spencer, A. Alavi, and G. Kresse, Journal of chemical theory and computation 7, 2780 (2011).
- [215] L. Frediani and D. Sundholm, Physical Chemistry Chemical Physics 17, 31357 (2015).
- [216] S. M. Parker and T. Shiozaki, The Journal of chemical physics 141, 211102 (2014).
- [217] E. M. Stoudenmire and S. R. White, Phys. Rev. Lett. 119, 046401 (2017).
- [218] E. Schrödinger, Phys. Rev. 28, 1049 (1926).
- [219] E. H. Lieb, Int. J. Quantum Chem. 24, 243 (1983).
- [220] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
- [221] A. D. Becke, J. Chem. Phys. 98, 5648 (1993).
- [222] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [223] J. P. Coe, K. Capelle, and I. D'Amico, Phys. Rev. A 79, 032504 (2009).
- [224] M. Levy and J. Perdew, Phys. Rev. A 32, 2010 (1985).
- [225] J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, The Journal of Chemical Physics 123, 062201 (2005).
- [226] J. P. Perdew and M. Levy, Phys. Rev. Lett. 51, 1884 (1983).
- [227] L. J. Sham and M. Schlüter, Phys. Rev. Lett. 51, 1888 (1983).
- [228] C. O. Almbladh and A. C. Pedroza, Phys. Rev. A 29, 2322 (1984).
- [229] K. Laidig, Chem. Phys. Lett. 225, 285 (1994).
- [230] C. Filippi, C. J. Umrigar, and M. Taut, The Journal of Chemical Physics 100, 1290 (1994).
- [231] R. M. Q. Zhao and R. Parr, Phys. Rev. A 50, 2138 (1994).
- [232] A. Görling and M. Levy, Int. J. Quant. Chem. 29, 93 (1995).
- [233] C. Filippi, X. Gonze, and C. J. Umrigar, *Recent Developments and Applications of Density Functional Theory*, edited by J. M. Seminario (Elsevier, Amsterdam, 1996) pp. 295–326.
- [234] R. Leeuwen, O. V. Gritsenko, and E. J. Baerends, in *Density Functional Theory I*, Topics in Current Chemistry, Vol. 180, edited by R. Nalewajski (Springer Berlin Heidelberg, 1996) pp. 107–167.
- [235] O. Gritsenko and E. Baerends, Phys.Rev. A 54, 1957 (1996).
- [236] M. Thiele, E. K. U. Gross, and S. Kümmel, Phys. Rev. Lett. 100, 153004 (2008).

- [237] C. Verdozzi, Phys. Rev. Lett. 101, 166401 (2008).
- [238] S. R. White, Phys. Rev. Lett. 69, 2863 (1992).
- [239] S. R. White, Phys. Rev. B 48, 10345 (1993).
- [240] U. Schollwöck, Rev. Mod. Phys. 77, 259 (2005).
- [241] E. Cancès and C. Le Bris, ESAIM: Mathematical Modelling and Numerical Analysis **34**, 749 (2000).
- [242] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (Dover Publishing, Mineola, New York, 1996).
- [243] C. J. Umrigar and M. Nightingale, Quantum Monte Carlo Methods in Physics and Chemistry, Vol. 525 (Springer, 1999).
- [244] H. Englisch and R. Englisch, Physica A: Statistical Mechanics and its Applications 121, 253 (1983).
- [245] M. Levy, Phys. Rev. A 26, 1200 (1982).
- [246] R. van Leeuwen (Academic Press, 2003) pp. 25 94.
- [247] A. Görling, Phys. Rev. A 46, 3753 (1992).
- [248] Y. Wang and R. G. Parr, Phys. Rev. A 47, R1591 (1993).
- [249] P. R. T. Schipper, O. V. Gritsenko, and E. J. Baerends, Theoretical Chemistry Accounts: Theory, Computation, and Modeling (Theoretica Chimica Acta) 98, 16 (1997), 10.1007/s002140050273.
- [250] K. Peirs, D. Van Neck, and M. Waroquier, Phys. Rev. A 67, 012505 (2003).
- [251] R. M. Dreizler and E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer–Verlag, Berlin, 1990).
- [252] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, eds., *Numerical Recipes*, 3rd ed. (Cambridge University Press, New York, 2007).
- [253] W. Kohn, Phys. Rev. Lett. 51, 1596 (1983).
- [254] C. Broyden, Mathematics of Computation 19, 577 (1965).
- [255] V. R. Saunders and I. H. Hillier, International Journal of Quantum Chemistry 7, 699 (1973).
- [256] A. D. Daniels and G. E. Scuseria, Phys. Chem. Chem. Phys. 2, 2173 (2000).
- [257] L. Thogersen, J. Olsen, D. Yeager, P. Jorgensen, P. Salek, and T. Helgaker, The Journal of Chemical Physics 121, 16 (2004).

- [258] J. B. Francisco, J. M. Martinez, and L. Martinez, The Journal of Chemical Physics 121, 10863 (2004).
- [259] C. Yang, J. Meza, and L. Wang, SIAM Journal on Scientific Computing **29**, 1854 (2007), http://epubs.siam.org/doi/pdf/10.1137/060661442.
- [260] J. P. Perdew and M. Levy, Phys. Rev. B 31, 6264 (1985).
- [261] J. P. Perdew, International Journal Of Quantum Chemistry 28, 497 (1985).
- [262] M. A. Buijse, E. J. Baerends, and J. G. Snijders, Phys. Rev. A 40, 4190 (1989).
- [263] N. Helbig, I. V. Tokatly, and A. Rubio, J. Chem. Phys. 131, 224105 (2009).
- [264] D. G. Tempel, T. J. Martínez, and N. T. Maitra, Journal of Chemical Theory and Computation 5, 770 (2009).
- [265] M. Fuchs, Y.-M. Niquet, X. Gonze, and K. Burke, The Journal of Chemical Physics **122**, 094116 (2005).
- [266] E. K. U. Gross and K. Burke, Lect. Notes Phys 706, 1 (2006).
- [267] J. C. Slater, Phys. Rev. 34, 1293 (1929).
- [268] L. Armijo, Pacific J. Math. 16, 1 (1966).
- [269] C. A. Ullrich, *Time-Dependent Density-Functional Theory* (Oxford University Press, Oxford, 2012).
- [270] M. Thiele and S. Kümmel, Phys. Rev. Lett. 112, 083001 (2014).
- [271] P. Gori-Giorgi and M. Seidl, Phys. Chem. Chem. Phys. 12, 14405 (2010).
- [272] A. D. Rabuck and G. E. Scuseria, The Journal of Chemical Physics 110, 695 (1999).
- [273] A. J. Cohen and P. Mori-Sánchez, arXiv:1308.1991 (2013).
- [274] N. T. Maitra, The Journal of Chemical Physics **122**, 234104 (2005).
- [275] M. A. Natiello and G. E. Scuseria, International Journal of Quantum Chemistry 26, 1039 (1984).
- [276] I. D'Amico, J. P. Coe, V. V. Franca, and K. Capelle, Phys. Rev. Lett. 106, 050401 (2011).
- [277] M. Maroun, *Generalized Quantum Theory and Mathematical Foundations of Quantum Field Theory* (University of California, Riverside, 2013) p. 69.
- [278] U. von Barth and L. Hedin, Journal of Physics C: Solid State Physics 5, 1629 (1972).
- [279] L. W. S. H. Vosko and M. Nusair, Can. J. Phys. 58, 1200 (1980).
- [280] R. Bauernschmitt and R. Ahlrichs, The Journal of Chemical Physics 104, 9047 (1996).

- [281] O. V. Gritsenko and E. J. Baerends, The Journal of Chemical Physics 120, 8364 (2004).
- [282] S. M. Valone, The Journal of Chemical Physics **73**, 4653 (1980).
- [283] C. A. Ullrich and W. Kohn, Phys. Rev. Lett. 87, 093001 (2001).
- [284] J. Chayes, L. Chayes, and M. Ruskai, Journal of Statistical Physics 38, 497 (1985).
- [285] J. W. Hollett and P. M. W. Gill, The Journal of Chemical Physics 134, 114111 (2011).
- [286] W. Rudin, *Principles of mathematical analysis*, Vol. 3 (McGraw-Hill New York, 1964).
- [287] R. Shankar, Principles of quantum mechanics (Springer Science & Business Media, 2012).
- [288] C. Garcia-Cervera, IPAM Book of DFT (2017).
- [289] M. Reed and B. Simon, *Methods of modern mathematical physics. vol. 1. Functional analysis* (Academic, 1980).
- [290] J. V. Neumann, *Mathematical foundations of quantum mechanics*, 2 (Princeton university press, 1955).
- [291] A. Messiah, "Quantum mechanics. vol. i.." (1958).
- [292] T. Kato, Transactions of the American Mathematical Society **70**, 195 (1951).
- [293] D. Ruelle, Il Nuovo Cimento A 61, 655 (1969).
- [294] W. Amrein and V. Georgescu, *Characterization of bound states and scattering states in quantum mechanics*, Tech. Rep. (Univ., Geneva, 1973).
- [295] V. Enss, Communications in Mathematical Physics 61, 285 (1978).
- [296] W. Hunziker, Helvetica Physica Acta (Switzerland) 39 (1966).
- [297] C. Van Winter, Kgl. Danske Videnskab. Selskab, Mat. Fys. Skrifer 2 (1964).
- [298] G. M. Zhislin, Trudy Moskovskogo Matematicheskogo Obshchestva 9, 81 (1960).
- [299] A. D. Becke, Phys. Rev. A 38, 3098 (1988).
- [300] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B 13, 4274 (1976).
- [301] K. Burke, IPAM Book of DFT (2017).
- [302] M. Levy, IPAM Book of DFT (2017).
- [303] J. P. Perdew, IPAM Book of DFT (2017).
- [304] S.-K. Ma and K. A. Brueckner, Phys. Rev. 165, 18 (1968).
- [305] D. C. Langreth and J. P. Perdew, Phys. Rev. B 21, 5469 (1980).

- [306] J. P. Perdew, Phys. Rev. B 33, 8822 (1986).
- [307] D. C. Langreth and M. Mehl, Phys. Rev. B 28, 1809 (1983).
- [308] J. P. Perdew and W. Yue, Phys. Rev. B 33, 8800 (1986).
- [309] J. A. Pople, Rev. Mod. Phys. 71, 1267 (1999).
- [310] W. Kohn, Rev. Mod. Phys. 71, 1253 (1999).
- [311] P. M. Gill, B. G. Johnson, and J. A. Pople, Chem. Phys. Lett. 209, 506 (1993).
- [312] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B 54, 16533 (1996).
- [313] E. H. Lieb and S. Oxford, Int. J. Quantum Chem. 19, 427 (1981).
- [314] F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, J. Chem. Phys. **109**, 6264 (1998).
- [315] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
- [316] J. P. Perdew and K. Schmidt, in *AIP Conference Proceedings* (IOP INSTITUTE OF PHYSICS PUBLISHING LTD, 2001) pp. 1–20.
- [317] J. P. Perdew, IPAM Book of DFT (2017).

Appendix A

The Quantum *N*-body problem

A.1 Overview

We discuss some basic properties of the Schrödinger equation. The discussion covers the role of self-adjointness and some spectral properties of the many-body Hamiltonian.

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A.2 Mathematical preliminaries

Before we discuss the quantum *N*-body problem, we introduce some basic mathematical concepts. We assume that the reader has some basic knowledge of linear algebra and analysis [286].

We begin with the definition of *metric* and *metric space*: Given a nonempty set *X*, a metric $d(\cdot, \cdot)$ on *X* is a function $d: X \times X \to \mathbb{R}$ with the following properties:

- 1. $d(x,y) \ge 0$ for all $x, y \in X$, and d(x,y) = 0 if and only if x = y.
- 2. d(x,y) = d(y,x) for all $x, y \in X$.
- 3. $d(x,y) \le d(x,z) + d(z,y)$ for all $x, y, z \in X$.

We denote by (X,d) a space X endowed with a metric d, and call it *metric space*. Note that one can typically define many different metrics on the same space X. The notion of metric generalizes the intuitive notion of distance between objects, and gives us a natural concept of *limit* and *convergence*: Let (X,d) be a metric space. Consider a sequence $\{x_n\}_{n\in\mathbb{N}} \subset X$, and $x \in X$. We say that $\{x_n\}_{n\in\mathbb{N}}$ converges to x (denoted $x_n \to x$) as n tends to infinity $(n \to \infty)$, if

$$\forall \varepsilon > 0, \exists n_0 \in \mathbb{N} \text{ such that } d(x_n, x) < \varepsilon \ \forall n \ge n_0.$$

We usually represent this by $\lim_{n\to\infty} x_n = x$. Given a sequence $\{x_n\}_{n\in\mathbb{N}}$ in a metric space (X,d), we often want to decide whether the sequence converges. The definition of limit that we just saw requires knowing what the limit of the sequence is, i.e., we need to know what x is, so that we cam measure the distance from the elements in the sequence to x. What we need is a condition that can guarantee that a limit exists, rather than a condition to verify that a certain given element is the limit. This is provided by the *Cauchy criterion* Let (X,d) be a metric space, and consider a sequence $\{x_n\}_{n\in\mathbb{N}} \subset X$. We say that $\{x_n\}_{n\in\mathbb{N}}$ satisfies the Cauchy criterion (or Cauchy condition) if

$$\forall \varepsilon > 0, \exists n_0 \in \mathbb{N} \text{ such that } d(x_n, x_m) < \varepsilon \ \forall n, m \ge n_0.$$

In such case we say that the sequence is a *Cauchy sequence*. Notice that this condition only involves knowledge of the sequence itself. It is clear that every convergence sequence satisfies the Cauchy criterion. The converse, however, is not true in general: We say that a metric space (X,d) is *complete* if every Cauchy sequence is convergent (in *X*). As an example, consider the space of

all rational numbers, \mathbb{Q} , and all real numbers, \mathbb{R} , with the usual metric given by the absolute value: d(p,q) = |p-q| for all $p,q \in \mathbb{Q}$. We know that every real number can be approximated by rational numbers, that is, for all $r \in \mathbb{R}$, there exists a sequence $\{q_n\}_{n \in \mathbb{N}} \subset \mathbb{Q}$ such that $\lim_{n \to \infty} q_n = r$. Therefore we see that (\mathbb{Q},d) is **not** complete. One can prove, however, that (\mathbb{R},d) is indeed complete [286].

A metric space does not necessarily have a liner structure, that is, we cannot add elements. From a physical point of view, this is important, given the *principle of superposition* [287]. Therefore we will consider vector spaces from now on. In this case, we can define the notion of *norm*: Given a vector space V over the complex numbers, \mathbb{C} , we define a norm, usually denoted by $\|\cdot\|$, as a function $\|\cdot\|: V \to \mathbb{R}$ with the following properties:

- 1. $||v|| \ge 0$ for all $v \in V$, and ||v|| = 0 if and only if v = 0.
- 2. $\|\alpha v\| = |\alpha| \|v\|$ for all $\alpha \in \mathbb{C}$ and all $v \in V$.

3.
$$||u+v|| \le ||u|| + ||v||$$
 for all $u, v \in V$.

We denoted by $(V, \|\cdot\|)$ the pair of a vector space and its norm, and we call it a *normed space*. Give a norm $\|\cdot\|$ on V, we can define the metric $d(u, v) = \|u - v\|$ for all $u, v \in V$. Thus, every normed space is a metric space, and we can define convergence. A *Banach space* is defined as a complete normed space.

Another important concept is that of an *inner product*. On a normed space we can measure distances, but not angles and other geometric properties, such as orthogonality. An inner product allows us to do this: Given a complex vector space V, an *inner product* (\cdot, \cdot) on V is a map $(\cdot, \cdot) : V \times V \to \mathbb{R}$ with the following properties:

- 1. $(u, u) \ge 0$ for all $u \in V$.
- 2. $(\alpha u + \beta v, w) = \alpha(u, w) + \beta(v, w)$ for all $u, v, w \in V$ and all $\alpha, \beta \in \mathbb{C}$.

3.
$$(u, v) = \overline{(v, u)}$$
 for all $u, v \in V$.

It follows from the last two condition that

$$(w, \alpha u + \beta v) = \overline{\alpha}(w, u) + \overline{\beta}(w, v) \quad \forall u, v, w \in V \text{ and } \forall \alpha, \beta \in \mathbb{C}.$$

Every inner product satisfies the **Cauchy-Schwarz inequality**: Let *V* be a vector space and (\cdot, \cdot) an inner product on *V*. Then

$$|(u,v)| \le (u,u)^{1/2} (v,v)^{1/2} \quad \forall u,v \in V.$$

It follows easily from this that the function $||u|| = (u, u)^{1/2}$ defines a norm on *V*. Another consequence of the Cauchy-Schwarz inequality is that we can define the angle $\theta \in [0, \pi]$, between to (nonzero) elements $u, v \in V$ by the relation

$$\cos(\theta) = \frac{(u,v)}{\|u\| \|v\|}.$$

We say that two vectors $u, v \in V$ are orthogonal if (u, v) = 0, i.e. if $\theta = \pi/2$.

We have seen that an inner product defines a norm; if with this norm, the space is complete, we say that it is a *Hilbert space*. An example of a Hilbert space that we will be using is $L^2(\mathbb{R}^3; \mathbb{C})$, that is, the space of all complex-valued Lebesgue measurable functions on \mathbb{R}^3 that are square integrable.

Operators

Let \mathscr{H} be a Hilbert space. An *operator* T on \mathscr{H} is a linear map $T : \mathfrak{D}(T) \to \mathscr{H}$, where $\mathfrak{D}(T)$, called the *domain* ot T, is a subspace of \mathscr{H} . We say that an operator $T : \mathfrak{D}(T) \to \mathscr{H}$ is bounded if $\exists M > 0 : ||Tu||_{\mathscr{H}} \leq M ||u||_{\mathscr{H}} \forall u \in \mathfrak{D}(T)$. We denote by $B(\mathscr{H})$ the space of all bounded operators

defined on \mathscr{H} . Given $T \in B(\mathscr{H})$, we can define

$$||T|| = \inf \{M > 0 \mid ||Tu|| \le M ||u|| \ \forall u \in \mathscr{H} \}.$$

One can prove that this defines a norm on $B(\mathcal{H})$, and that with this norm $B(\mathcal{H})$ is a Banach space.

We say that *T* is densely defined if $\mathfrak{D}(T)$ is dense in \mathscr{H} , i.e., if $\overline{\mathfrak{D}(T)} = \mathscr{H}$, where we denote by \overline{E} the closure of a set *E* [286]: Given a metric space (X,d), and a nonempty subset $E \subset X$, we denote by *E'* the set of all limit points of *E* in *X*. Then, the *closure* of *E* is the set $\overline{E} = E \cup E'$. It *T* is densely defined, then any element in \mathscr{H} can be approximated by a elements in $\mathfrak{D}(T)$: $\forall u \in \mathscr{H}, \exists \psi_n \in \mathfrak{D}(T)$ s.t. $\|\psi_n - u\|_{\mathscr{H}} \stackrel{n \to \infty}{\to} 0$. For example, the set of smooth, compactly supported complex-valued functions on \mathbb{R}^d , denoted $C_0^{\infty}(\mathbb{R}^d; \mathbb{C})$, is dense in $L^2(\mathbb{R}^d; \mathbb{C})$: Given $\psi \in L^2(\mathbb{R}^d; \mathbb{C})$ and $\varepsilon > 0$, we can find $\phi \in C_0^{\infty}(\mathbb{R}^d; \mathbb{C})$ such that $\|\psi - \phi\|_2 < \varepsilon$, where

$$\|\boldsymbol{\psi}-\boldsymbol{\phi}\|_2^2 = \int_{\mathbb{R}^d} |\boldsymbol{\psi}-\boldsymbol{\phi}|^2.$$

An operator T on \mathscr{H} that is bounded and densely defined can be extended it from $\mathfrak{D}(T)$ to \mathscr{H} in a unique way. Therefore, unbounded operators (that is, those that are **not** bounded), are typically defined on a proper subspace of \mathscr{H} .

If an operator T is densely defined, we can define the adjoint T^* as the maximal operator such that

$$(Tu,v) = (u,T^*v), \quad \forall u \in \mathfrak{D}(T), \quad \forall v \in \mathfrak{D}(T^*).$$
 (A.1)

The adjoint is defined on

$$\mathfrak{D}(T^*) = \{ u \in \mathscr{H} | \text{the map from } \mathfrak{D}(T) \to \mathbb{C} \text{ given by } v \to (Tv, u) \text{ is continuous} \}.$$
(A.2)
This definition involves quite a bit of mathematics. The idea is the following: If T is densely defined, the domain $\mathfrak{D}(T)$ is dense. Therefore the linear map l(v) = (Tv, u) can be extended from $\mathfrak{D}(T)$ to \mathscr{H} . We will continue to denote it by l. Given such a linear, continuous, functional, we can use the Riesz representation theorem, which says that in a Hilbert space, any linear functional is an inner product. This means that $\exists ! y \in \mathscr{H}$ such that

$$l(v) = (v, y) \quad \forall v \in \mathscr{H}.$$
(A.3)

We therefore define $T^*(u) = y$.

We say that a densely defined operator T is symmetric if its adjoint T^* is an extension of T, i.e., $\mathfrak{D}(T) \subset \mathfrak{D}(T^*)$ and

$$(Tu,v) = (u,Tv) \quad \forall u,v \in \mathfrak{D}(T)$$
 (A.4)

This is often denoted as $T \subseteq T^*$. We say that *T* is self-adjoint if $T = T^*$, that is, if $\mathfrak{D}(T) = \mathfrak{D}(T^*)$, and

$$(Tu,v) = (u,Tv) \quad \forall u,v \in \mathfrak{D}(T).$$
 (A.5)

We denote by $\mathscr{S}(\mathscr{H})$ the set of bounded, self-adjoint operators defined on $\mathscr{H}.$

As an example, consider the operators $T_1 = i\frac{d}{dx}$ on $L^2(\mathbb{R}^3)$, defined on $\mathfrak{D}(T_1) = C_0^{\infty}(\mathbb{R})$ having at most a finite number of derivatives, and $T_2 = i\frac{d}{dx}$, defined on $\mathfrak{D}(T_2) = H^1(\mathbb{R}) = \left\{ f \in L^2(\mathbb{R}) \mid \frac{df}{dx} \in L^2(\mathbb{R}) \right\}$ having a not infinite number of derivatives. The Sobolev space $H^1(\mathbb{R}^d)$ will appear later on when we discuss the many-body Hamiltonian. There are several ways to define it formally, see [288], for example. It is easy to check that T_1 is symmetric. Its adjoint is $T_1^* = i\frac{d}{dx}$, defined on $\mathfrak{D}(T_1^*) = H^1(\mathbb{R})$, that it, it is precisely T_2 . Therefore T_1 is symmetric, but not self-adjoint. the operator T_2 , on the other hand, is self-adjoint. One encounters this type of situation frequently, in which an operator can be seen formally to be symmetric by simple manipulations, such as integration by parts. The key to self-adjointness in such situations is whether the domain in which we have defined the operator and that of its adjoint are the same. Under some conditions, a symmetric operator can have a self-adjoint extension [289].

Self-adjointness is fundamental for the correct statistical interpretation of quantum mechanics, as shown by Von Neumann [290]. Furthermore, when discussing time-depending quantum systems, it is important to be able to define the quantum propagator $e^{it\hat{H}}$; it is precisely for self-adjoint operators that this can be defined and it forms a continuous group of unitary transformations. The equivalence of these two statements is precisely the content of Stone's theorem: Let \mathscr{H} be a Hilbert space, and $\{U(t)\}_{t\in\mathbb{R}}$ a family of unitary transformations on \mathscr{H} , i.e., $U(t) : \mathscr{H} \to \mathscr{H}$ for all $t \in \mathbb{R}$ such that ||U(t)x|| = ||x|| for all $x \in \mathscr{H}$. The family of unitary operators has the group property (i.e., U(t)U(s) = U(t+s) for all $t, s \in \mathbb{R}$) and is strongly continuous (i.e., $U(t) \to U(s)$ when $t \to s$), if and only if, there exists a self-adjoint operator \hat{H} on \mathscr{H} such that $U(t) = e^{it\hat{H}}$. Note that if an operator T on \mathscr{H} is bounded, the operator e^{itT} can be defined as a Taylor series. However, if T is unbounded this is no longer the case. If the operator is self-adjoint, e^{itT} can be defined via the spectral theorem [289].

A.3 The many-body Hamiltonian and Schrödinger's equation

We consider an isolated system of *N*-electrons and *K*-nuclei in the spinless, non-relativistic, Born-Oppenheimer approximation. Mathematically, such a quantum system is described by a state space \mathcal{H} , which is a complex Hilbert space, and a Hamiltonian \hat{H} , which is a self-adjoint operator on \mathcal{H} [290, 291].

Our Hilbert space will be

$$\mathscr{H} = L^2(\mathbb{R}^{3N}). \tag{A.6}$$

The state of the system is therefore represented by a wave function $\Psi \in L^2(\mathbb{R}^{3N})$. Since electrons are fermions, we require that Ψ be anti-symmetric, i.e.,

$$\Psi(\mathbf{r}_{\sigma(1)},\ldots,\mathbf{r}_{\sigma(N)})=(-1)^{\varepsilon_{\sigma}}\Psi(\mathbf{r}_{1},\ldots,\mathbf{r}_{N}),$$

for all permutations σ of $\{1, ..., N\}$, where ε_{σ} denotes its parity. We will denote by \mathscr{A} the set of antisymmetric wave-functions:

$$\mathscr{A} = \left\{ \Psi \in L^2(\mathbb{R}^{3N}) \mid \Psi \text{ is antisymmetric} \right\}.$$

The Hamiltonian is given by

$$\hat{H} = -\frac{1}{2} \sum_{i} \Delta_{i} + \sum_{i} v(\mathbf{r}_{i}) + \sum_{i < j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|},\tag{A.7}$$

where the external potential is defined as

$$\nu(\mathbf{r}) = -\sum_{\alpha=1}^{K} \frac{Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|},\tag{A.8}$$

for *K* nuclei with atomic charges $\{Z_{\alpha}\}_{\alpha=1}^{K}$ and positions $\{\mathbf{R}\}_{\alpha=1}^{K}$. However, much of what is presented applies to more general potentials.

Based on our previous discussion, we need to ask where we should define this operator, and whether it is self-adjoint. To understand this, we define the operator

$$\hat{H}_{0} = -\frac{1}{2} \sum_{i} \Delta_{i} + \sum_{i < j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}.$$
(A.9)

Kato [292] proved that \hat{H}_0 is self-adjoint in the space

$$\mathfrak{D}(\hat{H}_0) = H^2(\mathbb{R}^{3N}) \cap \mathscr{A} = \left\{ \Psi \in \mathscr{A} \mid \Delta \Psi \in L^2(\mathbb{R}^{3N}) \right\}.$$

The Kato-Rellich theorem states the following: Let \mathscr{H} be a Hilbert space, and let H_0 be a selfadjoint operator on \mathscr{H} with domain $\mathfrak{D}(H_0)$. Let V be a symmetric operator on \mathscr{H} that is *small relative to* H_0 , in the sense that $\mathfrak{D}(V) \subset \mathfrak{D}(H_0)$ and $\exists a, b > 0$ with a < 1 such that

$$\|Vu\| \leq a \|H_0u\| + b\|u\| \quad \forall u \in \mathfrak{D}(V).$$

Then $H = H_0 + V$ is self-adjoint on $\mathfrak{D}(H_0)$. If, in addition, H_0 is bounded below, so is H. As a consequence, since the Coulomb-type potential $v(\mathbf{r}) = -\sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{R}_{\alpha} - \mathbf{r}|}$ belogs to $L^2 + L^{\infty}$ (i.e., if $\exists v_1 \in L^2, v_2 \in L^{\infty}$ such that $v = v_1 + v_2$), one can prove that \hat{H} is self-adjoint on $\mathfrak{D}(\hat{H}_0) = H^2 \cap \mathscr{A}$ [292].

The ground state energy of the system, $E_{g.s.}$, is

$$E_{\text{g.s.}} = \inf_{\substack{\psi \in \mathfrak{D}(H) \\ \|\psi\|=1}} (\psi, H\psi). \tag{A.10}$$

Note that since

$$-\int_{\mathbb{R}^{3N}}\overline{\Psi}\Delta\Psi=\int_{\mathbb{R}^{3N}}|\nabla\Psi|^2 \ \forall\Psi\in H^2(\mathbb{R}^{3N}),$$

the expression (A.10) makes sense in a larger domain, what is called the form domain Q(H). In this case, $Q(H) = H^1(\mathbb{R}^{3N}) \cap \mathscr{A}$, which is often denoted as $\bigwedge_{i=1}^N H^1(\mathbb{R}^{\not\models})$. One can show that

$$E_{\text{g.s.}} = \inf_{\substack{\psi \in \mathcal{Q}(H) \\ \|\psi\|=1}} (\psi, \hat{H}\psi). \tag{A.11}$$

Note that, for a general potential even if $E_{g.s.} > -\infty$, there might not be a ground state; for example,

take the case v = 0, in which case \hat{H} reduces to \hat{H}_0 . If there is a ground state, though, then it satisfies the equation

$$\hat{H}\boldsymbol{\psi} = E_{\text{g.s.}}\boldsymbol{\psi}, \qquad \boldsymbol{\psi} \in \mathfrak{D}(\hat{H}), \, \|\boldsymbol{\psi}\| = 1. \tag{A.12}$$

A.4 Spectrum and Spectral Properties

Given an operator T on a Hilbert space \mathscr{H} , defined on $\mathfrak{D}(T)$, we define its range as $\mathscr{R}(T) = \{Tu \mid u \in \mathfrak{D}(T)\}$. The resolvent set of an operator T on the Hilbert space \mathscr{H} is the set $\rho(T) = \{\xi \in \mathbb{C} \mid (T - \xi \hat{1}) : \mathfrak{D}(T) \to \mathscr{R}(T - \xi \hat{1}) \text{ has an inverse}, (T - \xi \hat{1})^{-1} \text{ is continuous, and } \mathscr{R}(T - \xi \hat{1}) \text{ is dense in } \mathscr{H}\}$. Therefore, if $\xi \in \rho(T)$, the inverse $(T - \xi \hat{1})^{-1}$ can be extended continuously to \mathscr{H} . The spectrum of T is the complement of the resolvent set: $\sigma(T) = \mathbb{C} \setminus \rho(T)$.

If the operator T is self-adjoint and bounded below by E_{gs} , then $\sigma(T) \subseteq [E_{g.s.}, +\infty)$.

There are several decompositions of the spectrum and the nomenclature is not always consistent in the literature. We define the point spectrum,

$$\sigma_p(T) = \{ \xi \in \mathbb{C} | \exists \psi \neq 0, \ \psi \in \mathfrak{D}(T) \text{ such that } (T - \xi \hat{1}) \psi = 0 \}.$$
(A.13)

These are the eigenfunctions, or in short, e-functions.

We define the continuous spectrum as

$$\sigma_{c}(T) = \{ \xi \in \mathbb{C} | \exists (T - \xi \hat{1})^{-1} : \mathscr{R}(T - \xi \hat{1}) \to \mathscr{H}, \mathscr{R}(T - \xi \hat{1}) \text{ is dense, but } (T - \xi \hat{1})^{-1} \text{ is not continuous} \}$$
(A.14)

And we define the residual spectrum

$$\sigma_r(T) = \{\xi \in \mathbb{C} | \exists (T - \xi \hat{1})^{-1} \text{ but its domain } \mathscr{R}(T - \xi \hat{1}) \text{ is not dense} \}.$$
(A.15)

For self-adjoint operators, $\sigma_r(T) = \{\emptyset\}$.

Note that the spectrum is the disjoint union of these sets:

$$\sigma(T) = \sigma_p(T) \cup \sigma_c(T) \cup \sigma_r(T)$$
(A.16)

We can also distinguish the discrete spectrum,

$$\sigma_d(T) = \{ \xi \in \mathbb{C} | \xi \in \sigma_p(T) \text{ where } \xi \text{ is isolated with finite multiplicity} \}$$
(A.17)

The complement of the discrete spectrum is called the essential spectrum:

$$\sigma_{\rm ess}(T) = \sigma(T) \setminus \sigma_d(T) \tag{A.18}$$

A result due to Kato [292] shows that if $H = H_0 + V$, H_0 is self-adjoint and V is compact and symmetric, then H is self-adjoint and has the same essential spectrum as H_0 .

What is the physical meaning of the spectrum? This can be made precise as follows. Consider \mathscr{H}_B the closure of the subspace spanned by all eigenvectors of \mathscr{H} and $\mathscr{H}_C = \mathscr{H}_B^{\perp}$ its orthogonal complement; this means that $\mathscr{H} = \mathscr{H}_B \oplus \mathscr{H}_C$. We can define $\sigma_p(T) = \sigma(T|_{\mathscr{H}_B})$ and $\sigma_{\text{cont}}(T) = \sigma(T|_{\mathscr{H}_C})$. The first set is the point spectrum; the second set is a different notion of *continuous* spectrum often found in textbooks, and it differs from the previous one. Note that these sets may not be disjoint.

The following theorem, often referred to as the *RAGE Theorem* due to its contributors Ruelle [293], Amrein and Georgescu [294] and Enss [295], provides a precise statement about what eah subspace represents: Let T be a self-adjoint operator on $L^2(\mathbb{R}^d)$ with the local compactness properties, that is,

$$(\forall f \subset L^{\infty}, f(\mathbf{r}) \to 0, |\mathbf{r}| \to \infty \text{ then } f(\mathbf{r}).(H - \xi \hat{1})^{-1} \text{ compact } \forall \xi \in \rho(H).$$
 (A.19)

Let χ_R be the characteristic function of a ball of radius R > 0, i.e.,

$$\chi_R(\mathbf{r}) = \begin{cases} 1 & \text{if } \|\mathbf{r}\| < R, \\ 0 & \text{otherwise.} \end{cases}$$

Then:

$$\varphi \in \mathscr{H}_B \Leftrightarrow \lim_{R \to \infty} \|(1 - \chi_R)e^{-it\mathscr{H}}\varphi\| = 0 \tag{A.20}$$

uniformly in the range $0 \le t < \infty$.

Furthermore,

$$\varphi \in \mathscr{H}_c \Leftrightarrow \lim_{t \to \infty} \frac{1}{t} \int_0^t \|\chi_R e^{-isH} \psi\|^2 ds = 0 \quad \forall R \subset +\infty$$
(A.21)

Therefore, the space \mathcal{H}_B corresponds to what we intuitively call *bound states*, and the space \mathcal{H}_C corresponds to the *scattering states*.

A.4.1 The spectrum of \hat{H}

An important result is what is called the *HVZ Theorem*, due to Hunziker [296], van Winter [297], and Zhislin [298], and it describes the structure of the spectrum of the many-body Hamiltonian. We will denote the Hamiltonian in the following by \hat{H}_N , in order to indicate the number of electrons in



Figure A.1: A diagram of spectra as formalized in the HVZ theorem. A discrete set of eigenvalues in σ_d turns into a continuum past Σ in the σ_{ess} domain.

the system. The HVZ theorem states that if $N \leq Z = \sum_{\alpha=1}^{K} Z_{\alpha}$,

$$\sigma_d(\hat{H}_N) = \left\{ E_N^0 \le E_N^1 \le \cdots \le E_N^k \le \dots \right\},\,$$

and

$$\sigma_{\mathrm{ess}}(\hat{H}_N) = [\Sigma_N, \infty),$$

for some constant $\Sigma_N \ge \sup_k \{E_N^k\}$. Schematically, the spectrum of \hat{H}_N looks like Fig. A.1, and it means, for example, that the many-body Hamiltonian captures the physical picture of a molecule with infinitely many energy levels.

Furthermore, one can prove that the eigenvalues $\{E_N^k\}_{k=1}^{\infty}$ accumulate only at Σ_N , and if $N \ge 2$, then

$$\Sigma_N = E_{N-1}^0.$$

A.5 Conclusion

Quantum mechanics is based on operators which produce observables. In order to properly define sufficient operators to give observables that give finite values, we have introduced the concept

of self-adjointness. Physics texts introduce Hermitian operators but do not define the difference between symmetric and self-adjoint operators, the former being defined on the same domain as its adjoint and the latter being also onto. Self-adjoint operators are sufficient for defining a spectral theory and ensuring quantum mechanics is well defined.

Appendix B

History of the Generalized Gradient Approximation

B.1 Overview

Up to this point, we have explicitly avoided constructing arguments for better approximate functionals. Part of this is practical: for the case of our one dimensional model, the class of functionals beyond the LDA special consideration beyond what is derived in the three dimensional case. Consider the Becke-88 functional which relies on an asymptotic behavior of the high Z atoms [299]. This is not available for the exponential interaction since it does not bind all neutral atoms. However, it is important to understand where approximations fit in the context of the exact functional, since a thorough understanding of them will provide a context for us to use the knowledge gleaned from the investigation in the previous chapters.

In the construction of approximate density functionals, the natural next ingredient beyond the local density and local spin polarization is the density gradient. The second-order density gradient expansion of the exchange-correlation energy is the leading correction to the local density approximation (LDA) for a density that varies slowly over space, and might have been expected to provide a systematic improvement for real systems. Instead it was systematically worse for the correlation energy. This was explained by the fact that the gradient expansion of the exchange-correlation hole density can violate exact constraints that LDA satisfies, being better than LDA for the hole density close to an electron but seriously worse far away. Cutting off the spurious long-range parts of the gradient-expansion hole to recover the exact constraints led to the first generalized gradient approximations (GGAs). Later GGAs were fitted to appropriate norms like atoms, or to exact constraints on the energy functional. But the GGA form was still too limited to avoid a dilemma: A single GGA cannot simultaneously yield accurate bond lengths and accurate binding energies.

This retrospective offers some insight into how GGAs were developed for real systems.

This paper was authored with and given permission to be used here by John Perdew. It was submitted as part of the Institute for Pure and Applied Mathematics summer school on *Putting the theory back in density functional theory*.

B.2 Background

At the beginning of electronic structure theory, before the 1970s, calculations were severely limited by the computational power available then. They often started from the simplified Hartree approximation where $E_{\rm XC} = 0$. This approximation is cheap to calculate. It produces poor results, however. Typically, atoms are underbound to one another and lattice constants are too long.

The local spin density approximation (LSDA) can be summarized as an approximation to the exchange-correlation energy,

$$E_{\rm xc}^{\rm LSDA} = \int d\mathbf{r} \, n(\mathbf{r}) \mathcal{E}_{\rm xc}^{\rm unif}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})). \tag{B.1}$$

Note that $\int d\mathbf{r} n(\mathbf{r})$ is the number of electrons *N* and ε_{xc}^{unif} is the energy density per particle for the uniform gas. This approximation produces better results over the Hartree approximation. LSDA does much better at binding one atom to another. Typical errors are a few percent including lattice constants and binding energies. LSDA overbinds slightly in a wide variety of cases.

The key difference between the Hartree and LSDA approximations lies in the conditional probability [300, 301]. The Hartree approximation assumes that the probability of finding an electron at a second location is independent of the first location at which an electron was found immediately before, but the LSDA takes such a dependence into account.

So, LSDA is a good starting point–albeit not perfect.

B.3 Moving from local approximations to gradient approximations

Most chemists did not like the LSDA. More accurate functionals were needed. They wanted accurate results to better than 1%, though condensed matter physicists used it widely. Chemists are typically interested in precise measurements, so their wavefunction theories tended to beat the accuracy of LSDA.

A natural next step beyond LSDA is to add another local ingredient: the gradient of the local density.

B.3.1 Guiding principles of generalized gradient approximations

Three golden rules were needed to construct better density functionals non-empirically.

1. Get the uniform gas limit correct

This doesn't go beyond the LSDA, but it is a good starting point (beyond the Hartree approximation in particular).

2. Satisfy more exact constraints

Many were introduced by Mel Levy [302]. Other considerations are hidden constraints (see LDA lecture [303]).

3. Add more ingredients that provide more information

For example, moving from LDA to LSDA, one implements $n \to n_{\uparrow}, n_{\downarrow}$ This gives the functional more information and therefore more accuracy in calculating, for example, binding energies.

This list is not meant to be exhaustive. It simply presents some guiding principles that were used to move on from LSDA.

B.3.2 Density gradient approximation

Going back to Hohenberg-Kohn [1], we can attempt to construct the density functional as the result of a power series, with a small parameter proportional to $|\nabla n|/n$. For a density that varies slightly over space, a density-gradient-dependent functional may be found

$$E_{\rm XC}^{\rm GE2}[n] = \int d\mathbf{r} \left\{ n \, \varepsilon_{\rm XC}^{\rm unif}(n) + B_{\rm XC}(n) \frac{|\nabla n|^2}{n^{4/3}} \right\}$$
(B.2)

where GE2 refers to the gradient expansion to second order in perturbation theory. Spin indices and the density dependence on **r** have been suppressed until needed, and $B_{\rm XC}(n) = B_{\rm X} + B(n)$. Note that the coefficient for exchange, $B_{\rm X}$, is not density dependent based on scaling relations (see Levy lecture [302]) while the coefficient for $B_{\rm X}$ is since it has no equivalent scaling equality. The form of this expression was given by Ma and Bruckner [304] originally, with later understanding provided by Langreth and Perdew [305, 306]. The general strategy to determine these coefficients is to start from the uniform gas and apply a slowly varying potential. From second-order perturbation theory, the potential can be eliminated in terms of the density which produces the result. For *B*, one must start from the random phase approximation (RPA).

But the correlation energy of a real system is positive when this procedure is used. This is not physical. It is known that the exchange hole should be negative everywhere while the correlation hole can be positive or negative and both possess a damped and constrained long-range behavior. The exchange hole density should integrate to -1, and the correlation hole density to 0. When the two coordinates of the hole \mathbf{r} and $\mathbf{r'}$ are far apart, this expansion worsens since it does not capture these features.

Langreth and Perdew [305, 306] explained this as follows. Gradient expansions of the exchangecorrelation energy also correspond to expansions of the hole density. The second-order gradient expansion of $n_{\rm XC}(\mathbf{r}, \mathbf{r}')$ is not the XC hole of any possible physical configuration. This loses the exact constraints on $n_{\rm XC}$ that LDA satisfied. The second-order gradient expansion improves the hole over LDA only in the region close to the electron that the hole surrounds.

For the generalized gradient approximation (GGA), [307]

$$E_{\rm xc}^{\rm GGA}[n] = \int d\mathbf{r} \, n \, \varepsilon_{\rm xc}^{\rm GGA}(n, \nabla n) \tag{B.3}$$

where $\varepsilon_{\rm XC}^{\rm GGA}$ has all the higher orders of ∇n like $|\nabla n|^4$, $|\nabla n|^6$, $|\nabla n|^8$,.... An enhancement factor, $F_{\rm XC}$, over the local exchange can be defined by

$$E_{\rm XC}^{\rm GGA}[n] = \int d\mathbf{r} F_{\rm XC}(n, |\nabla n|) \, n \, \varepsilon_{\rm X}^{\rm unif}(n). \tag{B.4}$$

The first attempt to find a suitable form for $F_{\rm XC}$ was by Langreth and Mehl [307]. It recovers

the GE2 only when $|\nabla n|/n$ is small enough. Another GGA was constructed by Perdew and Wang [308]. These early GGAs were based on starting from the gradient expansion of the hole, $n_{\text{XC}}(\mathbf{r}, \mathbf{r}')$, by cutting off the spurious long range parts and satisfying the sum rules for n_{X} and n_{x} . On integration we would then find numerically $\mathcal{E}_{\text{XC}}^{\text{GGA}}(n, |\nabla n|)$ and parameterize the result as an analytic function of *n* and $|\nabla n|$.

B.3.3 Results

Compared to LSDA, the spin-density GGA:

- 1. reduces overbinding energies, but not enough
- 2. increases bond lengths but by too much

There is some difference between GGAs, some are better for binding energies by being worse for bond lengths or vice versa. This dilemma seems to be a consequence of the overly-limited GGA form of Eq. B.3.

Chemists moved to DFT largely based on seeing how effective and quick a computation with a GGA is compared to Hartree Fock. In fact, at a meeting in 1983 in Menton, Mel Levy and Axel Becke spoke with John Pople, who led the field in wavefunction methods and shared the Nobel prize with Walter Kohn in 1998 [309, 310]. Pople was convinced to try DFT methods and was pleased by the GGA results [311]. The floodgates opened, and DFT became as widely used in chemistry as in condensed matter physics.

B.3.4 Current Approach

A slew of exact constraints is available. Many exist for the functional itself instead of the hole. This made a new path. We satisfy exact constraints on $E_{\rm XC}[n]$, not on $n_{\rm XC}$ necessarily. The Perdew-Burke-Ernzerhof (PBE) [222, 312] was a transitional functional in that regard. Two derivations gave the same result in that case:

- 1. Cutoffs in real space of the second-order gradient expansions for the hole densities, including correlation as well as exchange.
- 2. Satisfaction of exact conditions
 - Recovery of the uniform density limit
 - Negativity of exchange and correlation energies
 - Recovery of the gradient expansion for correlation
 - Correct static linear response of the density at long wavelength
 - Uniform scaling equality for exchange and inequality for correlation
 - High density limit of the correlation energy
 - Lieb-Oxford lower bound [313] on the exchange-correlation energy

All hole cutoffs were done consistently in real space.

Other GGAs can be constructed by fitting to the energies of atoms, *e.g.* B88 [299], or of molecules (*e.g.*, Ref. [314]). GGAs can be compared by comparing their enhancement factors $F_{\rm XC}(n, |\nabla n|)$ over local exchange.

Note that to satisfy the uniform scaling conditions,

$$F_{\mathbf{X}}(n, |\nabla n|) = F_{\mathbf{X}}(s) \tag{B.5}$$



Figure B.1: Sketch of the exchange enhancement factor $F_x(s)$ for the PBE GGA. Note that the range $0 < s \le 3$ contributes significantly to important energy differences.

where

$$s = \frac{|\nabla n|}{2k_f n} = \frac{|\nabla n|}{2(3\pi^2)^{1/3} n^{4/3}}$$
(B.6)

which is the reduced or dimensionless density gradient, with $k_f = (3\pi^2 n)^{1/3}$.

LDA and GGA are computationally efficient and useful, but of limited accuracy. GGAs cannot simultaneously recover GE2 for exchange and the linear response of the uniform gas.

GGAs cannot simultaneously recover the second-order gradient expansion for exchange and accurate binding curves. PBE96 is a remarkable compromise. PBEsol is good for lattice constants but not for binding energies [315].

B.3.5 Jacob's ladder of density functional approximations

A trade-off appears when considering functionals that contain more ingredients. Simpler functionals cost less to evaluate, but they offer less accuracy than functionals containing more ingredients. This can be summarized by examining Jacob's ladder of density functional approximations [316],



Figure B.2: Jacob's ladder represents the levels of approximation for the density functional. Going up the ladder adds more ingredients, giving more accuracy, but also increases the cost. LDA includes only the value of the local density while GGAs include gradients as well. Meta-GGAs includes kinetic energy densities $\tau = \sum_i |\nabla \phi_i|^2/2$. Functionals not in the semilocal category include hybrids which mix exact exchange into the functional. RPA-like functionals can be used but at great cost. If one could go one step higher, then the exact functional would be achieved. The step below LDA is the very inaccurate Hartree approximation.

shown in Fig. B.2. At the lowest rung, LDA includes only the local density *n* to construct the XC energy density at **r**. The next rung is occupied by GGAs which use both *n* and ∇n . This comes at a far greater accuracy than LDA.

Including kinetic energy densities gives the meta-GGA [317]. The next rung includes hybrid functionals, but these require the evaluation of exact exchange and thus an increased cost. The last rung comprises methods related to the random phase approximation (RPA) which include unoccupied orbitals. These come at an even larger cost but improved accuracy.

B.4 Conclusion

Density functionals have a long history of steady improvement. Each time more information from exact constraints and appropriate norms is used, the functionals become better approximations.

The move from the overly crude Hartree approximation to using the local density approximation improved results, but not to chemical accuracy. The move from the local density approximation to include gradients-and in particular generalized gradient approximations based on satisfying exact sum rules-made functionals accurate enough for comparison with chemical experiments. Hence, they are widely used.