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RPPR Final Report
as of 17-Aug-2018

Agency Code:

Proposal Number: 56816PHSR **Agreement Number: W911NF-04-D-0003**
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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: **STEM Participants:**

Major Goals: QMC calculations of molecular systems. The emphasis has been on several important and related research questions: calculations of properties beyond energies such as dipole moments; calculations of excited states; accuracy of pseudopotentials; impact of many-body effects and interactions beyond repulsive terms, bonding and electronic densityon accuracy of fermion nodal surfaces; and number of related topics that have to do with technical points of such calculations.

We studied behavior of ultracold atomic Fermi gases. In particular, we carried out high accuracy quantum Monte Carlo calculations for spin unpolarized unitary limit systems using the Bardeen-Cooper-Schrieffer (BCS) pairing wavefunctions and extrapolations of the interaction potential to zero range (ie, the true unitary limit).

Accomplishments: See attached.

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

ARTICLES:

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
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Article Title: Precision benchmark calculations for four particles at unitarity
Authors:
Keywords: Unitarity limit
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Authors:
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Authors:
Keywords: QMC, azobenzene, optically active
Abstract:
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Article Title: Study of dipole moments of LiSr and KRb molecules by quantum Monte Carlo methods
Authors:
Keywords: QMC, dipole moment, LiSr, KBr, polar molecules, fixed-nodeapproximation, electron correlation
Abstract: We calculate the Born-Oppenheimer potential energy and electric dipole moment as a function of internuclear separation for two diatomic molecules, LiSr and KRb. These molecules are of interest to experiments exploiting ultracold polar molecules in a number of novel ways. Here we apply correlated approaches such as high-accuracy quantum Monte Carlo for calculations of selected molecular properties in an explicitly many-body manner. We use small- core effective potentials combined with multi-reference Slater-Jastrow trial wave functions to provide accurate nodes for the fixed-node diffusion Monte Carlo method. For reference and comparison, we calculate the same properties with Hartree-Fock and restricted Configuration Interaction methods and carefully assess the impact of the recovered many-body correlations on the calculated quantities.
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Article Title: Variational Monte Carlo for spin-orbit interacting systems
Authors:
Keywords: VMC, diffusion Monte Carlo, spin-orbit coupling, Rashba coupling,
Abstract: Recently, a diffusion Monte Carlo algorithm was applied to the study of spin dependent interactions in condensed matter. Following some of the ideas presented therein, and applied to a Hamiltonian containing a Rashba-like interaction, a general variational Monte Carlo approach is here introduced that treats in an efficient and very accurate way the spin degrees of freedom in atoms when spin orbit effects are included in the Hamiltonian describing the electronic structure. We illustrate the algorithm on the evaluation of the spin-orbit splittings of isolated C, Tl, Pb, Bi, and Po atoms. In the case of the carbon atom, we investigate the differences between the inclusion of spin-orbit in its realistic and effective spherically symmetrized forms. The method exhibits a very good accuracy in describing the small energy splittings, opening the way for a systematic quantum Monte Carlo studies of spin-orbit effects in atomic systems.
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Final Report for the project: Quantum Monte Carlo Simulations

GRANT NUMBER: W911NF-04-D-0003-0012, Army Research Office

Period: 2009-2014

INSTITUTION: North Carolina State University, Department of Physics

PRINCIPAL INVESTIGATOR(S): Lubos Mitas, NCSU

Peter J. Reynolds, ARO (staff research)

Research accomplishments:

We have worked on the following research directions. In particular:

i) QMC calculations of molecular systems. The emphasis has been on several important and related research questions: calculations of properties beyond energies such as dipole moments; calculations of excited states; accuracy of pseudopotentials; impact of many-body effects and interactions beyond repulsive terms, bonding and electronic densityon accuracy of fermion nodal surfaces; and number of related topics that have to do with technical points of such calculations. One the main topics was the calculations of energies and dipole moments for I-II diatomic molecules LiSr and KRb. This has been motivated due to their relevance to optical lattice experiments with further perspectives on studies of phase transitions as well their potential for as quantum computing application. Results have been computed by quantum Monte Carlo and compared with restricted CI calculations. We found in both cases that correlation effects smooth-out and decrease the amplitudes of the dipole moments when compared with the reference/mean-field Hartree-Fock calculation. The optimization of the trial functions for quantum Monte Carlo proved quite challenging, especially for the LiSr case which shows significant changes in the electronic structure as a function of the bond length. This is due to the complicated bond structure with the doublet ground state and one electron occupying an antibonding orbital. This results in the sign change of the dipole moment close to the equilibrium bond length, and restructuring of the low-lying excitations, which affect the construction of the accurate trial functions. These calculations relied on a number of studies that enabled better to understand the intricacies of many-body effects in molecular and other many-particle fermionic systems. This included variety of tests such a) we increased the size of basis set to the saturated limit, b) we employed newly derived and tabulated pseudopotentials for Sr, K, and Rb, c) we recalculated Configuration Interaction wavefunctions with the largest feasible active spaces which included single, double and triple excitations d) we recalculated the fixed-node energies within these updates, e) we investigated the accuracy of calculations of excited states. These calculations showed importance of checking all necessary

components that enter such calculations as it has been investigated directly or indirectly in several papers done in our groups as well as with collaborations as can be found in references [2,6,7,8,11-18].

ii) We studied behavior of ultracold atomic Fermi gases. In particular, we carried out high accuracy quantum Monte Carlo calculations for spin unpolarized unitary limit systems using the Bardeen-Cooper-Schrieffer (BCS) pairing wavefunctions and extrapolations of the interaction potential to zero range (ie, the true unitary limit). We have found lower energies than previously published values from fixed-node diffusion Monte Carlo calculations. For example, our Bertsch parameter for 66 particles is xi=E_tot/E_free = 0.395(2) as compared to values 0.40(3) - 0.44(3) published previously by other groups. We have calculated essentially an exact energy for the benchmark/testing 4-particle system by using highly accurate variational wave functions, fixed-node and released-node diffusion Monte Carlo methods. In addition, we explored the nodal release for 14-particle system but found essentially no improvement when using the best wave functions. We could identify a clear energy drop though when using suboptimal wave functions with distorted nodes. We have concluded that the BCS wave functions are very accurate for the unitary gas systems. Results were published in Ref. [1,4,5].

iii) We have carried out preliminary studies of treating electronic spins as quantum dynamical variables in QMC. This is important in several contexts: for systems with spintronics application potential (eg, quantum computing) and also for systems with significant contributions of spin-orbit interactions such as heavy elements. With collaborators from Italy we have made progress in carrying out variational calculations for few-electron systems based on previosuly introduced QMC methodology for Rashba spin-orbit interaction in 2D electron gas and variational Monte Carlo studies of atoms. The results were published in papers, Refs [9,10].

Publications in refereed journals:

[1] M. Bajdich, J. Kolorenc, L. Mitas, and P. J. Reynolds, Pairing in Cold Atoms and other Applications for Quantum Monte Carlo methods, Physics Procedia **3**, 1397–1410 (2010)

[2] M. Dubecky, R. Derian, L. Mitas and I. Stich, Ground and Excited Electronic States of Azobenzene: a QMC Study, J. Chem. Phys. 133, 244301 (2010)

[3] J. Kolorenc and L. Mitas, *Applications of quantum Monte Carlo in condensed systems*, Rep. Prog. Phys. **74**, 026502 (2011)

[4] Shahin Bour, Xin Li, Dean Lee, Ulf-G. Meißner, and Lubos Mitas, Precision benchmark calculations for four particles at unitarity, Phys. Rev. A **83**, 063619 (2011)

[5] Xin Li, Jindřich Kolorenč, and Lubos Mitas, Atomic Fermi gas in the unitary limit by quantum Monte Carlo methods: Effects of the interaction range, Phys. Rev. A **84**, 023615 (2011)

[6] L. Horvathova, Dubecky, M., Mitas, L., and Stich, I., Spin multiplicity and symmetry breaking in vanadium- benzene complexes, Phys. Rev. Lett., **109**, 053001 (2012)

[7] K.M. Rasch, and Mitas, L. Impact of electron density on the fixed-node errors in quantum Monte Carlo, Chem. Phys. Lett., **528**, 59 (2012)

[8] S. Hu, Rasch, K., and Mitas, L. Many-body nodal hypersurface and domain averages for correlated wave functions. In Advances in Quantum Monte Carlo, Editor(s): Shigenori Tanaka, Stuart M. Rothstein, William A. Lester , Jr., ACS Symposium Series, Volume 1094, American Chemical Society, (peer reviewed book chapter), pp 77-87 (2012)

[9] A. Ambrosetti, F. Pederiva, E. Lipparini, L.Mitas, Quantum Monte Carlo in the presence of spin-orbit interactions. In Advances in Quantum Monte Carlo, Editor(s): S. Tanaka, S. M. Rothstein, W. A. Lester, Jr., ACS Symposium Series, Volume 1094, American Chemical Society, (peer rev.), pp. 119-130 (2012), Chap. 10

[10] Ambrosetti, A., Silvestrelli, P., Toigo, F., Mitas, L., and Pederiva, F. Variational Monte Carlo for spin-orbit interacting systems. Phys. Rev. B **85**, 045115 (2012)

[11] Shi Guo, Michal Bajdich, Lubos Mitas, Peter J. Reynolds, Study of dipole moments of LiSr and KRb molecules by quantum Monte Carlo methods, Molec. Phys. **111**, 1744 (2013)

[12] M. Zhu, L. Mitas, Quantum Monte Carlo study of effective core potentials accuracy for transition elements, Chem. Phys. Lett., **572**, 136 (2013)

[13] L. Horvathova, Dubecky, M., Mitas, L., and Stich, I., QMC study of energetics and structure of neutral and cationic vanadium-benzene half-sandwich, J. Chem. Theor. Comp., **9**, 390 (2013)

[14] M. Dubecky, P. Jurecka, R. Derian, P. Hobza, M. Otyepka, and L. Mitas, Quantum Monte Carlo describe noncovalent interactions with subchemical accuracy; J. Chem. Theor. Comp., **9**, 4287 (2013)

[15] M. Dubecky, R. Derian, P. Jurecka, L. Mitas, P. Hobza, and M. Otyepka, Quantum Monte Carlo for noncovalent interactions: an efficient protocol attaining benchmark accuracy, Phys. Chem. Chem. Phys, **16**, 20915-20923 (2014)

[16] L. Horvathova, R. Derian, L. Mitas, and I. Stich, Quantum Monte Carlo study of one-dimensional transition-metal organometallic cluster systems and their suitability as spin filters, Phys. Rev. B **90**, 115414 (2014)

[17] K. M. Rasch, S. Hu, and L. Mitas, Interplay of electron density and node nonlinearities, J. Chem. Phys. **140**, 041102 (2014)

[18] A. Kulahlioglu and L. Mitas, A quantum Monte Carlo study of zinc-porphyrin: Vertical excitation between the singlet ground state and the lowest-lying singlet excited state, Comput. Theor. Chem., **1046**, 6-9 (2014)

Presentations:

L. Mitas, invited presentations:

1. Invited seminar, Institute of Condensed Matter Theory, U. Illinois Urbana-Champaign, 2014
2. Invited Talk, NWChem Workshop, Seattle, 2014
3. Invited Colloquium, Palacky Univ., Olomouc, Czech Rep., 2014;
4. Invited Seminar, Workshop on 2D and graphene nanosystems, Slovak Academy of Sciences, Bratislava, Slovak Rep., 2014;
5. Invited Talk, INT, Advances in Quantum Monte Carlo Techniques for Non-Relativistic Many-Body Systems Workshop, U. Washington, Seattle,WA, 2013
6. Invited Talk and Colloquium, MASP2012, International School and Workshop, Kashiwa, Japan, 2012
7. Invited Talk, Materials Genome DOE Meeting, U. Southern California, LA, 2012
8. Invited Talk, CCP2011, Conference in Computational Physics, Gatlinburg, TN, 2011
9. Invited Talk, ACS General Meeting, Denver, CO, 2011
10. Invited Talk, Electronic Structure 2011 Workshop, University of Pennsylvania, Philadelphia, PA, 2011
11. Invited Seminar, LANL, Los Alamos, NM, 2010
12. Invited Talk, Pacifichem 2010, Hawaii, HI, 2010
13. Invited Talk, Correlated wavefunction methods in physics and chemistry, International Workshop, Lugano, Switzerland, 2010

Software:

Open Source Quantum Monte Carlo Package QWalk, www.qwalk.org

Technology Transfer/Patents/Inventions:

N/A