Accurate predictions of ionization and atomization energies without the Born-Oppenheimer approximation

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In this work we calculate the non-relativistic ground-state energies of atomic and molecular systems both with and without the Born Oppenheimer approximation. For this we utilize the fixed-node diffusion Monte carlo method, in which the nodes depend both on the electronic and ionic positions. We report ground state energies, ionization energies and atomization energies to an accuracy of $0.1 - 3.0$mHa. We find the ionization energies of the atoms to be independent of the adiabatic assumption, showing that the coupling between the nucleus and valence electrons is not important in the ionization process. The atomization energies, however, are significantly influenced by the non-adiabatic coupling of electrons and nuclei. We demonstrate that the fixed node approximation provides a highly accurate and scalable approach to treating molecule systems beyond the Born Oppenheimer approximation. Moreover, further development of this approach is discussed by considering a multi-time-step scheme for moving the ions.

I. INTRODUCTION

There has been several recent discoveries that suggest that quantum wave functions, which include both electronic and ionic degrees of freedom, have many interesting properties that have yet to be explored. This includes the development of equations that exactly factorize a wave function into electron and ionic components [1], the disappearance of conical intersections in wave functions of model systems [2], and the use of quantum entanglement to study electronic and ionic density matrices [3]. Extending such studies to realistic systems is of broad interest and will considerably expand our understanding of electron-ion systems. However, treatment of *ab initio* electron-ion systems is challenging and applications have thus been limited. The most accurate simulations of electron-ion wave functions are generally done with very specialized wave functions, which are limited to rather small systems sizes [4].

As a framework to address these problems in general realistic systems, we recently demonstrated that quantum Monte Carlo (QMC) can be combined with quantum chemistry techniques to generate electron-ion wave functions [5]. We treated realistic molecular systems and demonstrated that our method can be scaled to larger systems than previously considered while maintaining a highly accurate wave function. In the following we extend our previous work by considering the simulation of a larger benchmark set of atoms and molecules. We calculate ionization energies and dissociation energies which can be directly compared with previous benchmarking results. We also consider using multiple time steps for different species in the imaginary time propagator, which is also developed and tested. Additionally we consider other estimators and the errors associated by using a mixed estimator.

II. METHOD

A. Fixed-Node Diffusion Monte Carlo (FN-DMC)

Diffusion Monte Carlo is a projector method that evolves a trial wavefunction with a Hamiltonian in imaginary time and projects out the ground-state wavefunction. For practical simulations of fermions, the fixed-node approximation is introduced, which depends only on set of electronic positions where a trial wave functions is equal to zero. This approximation is different than approximations typically used in quantum chemistry calculations, and in this work we demonstrate that we can generate high quality nodal surfaces for full electron-ion wave functions. In the limiting case that the trial wavefunction has the same nodal surface as the exact ground-state wavefunction, the final ground-state energy will be exact. Approximate nodal surface can be generated through optimization of the full wave function. Such approximate nodal surfaces have been tested and validated on a wide range of systems, and consistently provide an excellent approximation of the exact ground-state energy, comparable to the state of the art in *ab initio* simulations [**refs. here**]. In addition the energies generated with FN-DMC are variational with regards to the ground state energy.

In all but a handful of previous QMC simulations, ions are "clamped" to their equilibrium positions. Such an assumption is not fundamentally required by FN-DMC. It is possible to optimize thousands of wave function parameters simultaneously with variational Monte Carlo [6–8] . In our previous work we found that the most important

effect to optimize for were the nodes due to electron-electron correlations [5], and in this regard we use more sophisticated electronic terms in the wave function than the ion part of the wave function.

B. Electron Wavefunction and Optimization

The are several different approaches for generating high quality wave functions [8–11]. We use an initial guess for the wavefunction that is generated from complete active space self-consistent field (CASSCF) [12, 13] calculation using the quantum chemistry package GAMESS [14]. The optimized orbitals are then used in a second order configuration interaction (SOCI) calculation to generate a series of configuration state functions (CSF) [15]. The multi-CSF expansion of the wavefunction can be expressed in the following form,

$$\Psi_{SOCI}(\vec{r}) = \sum_{i=1}^{N_{CSF}} \alpha_i \phi_i(\vec{r}), \tag{1}$$

where $\vec{r}$ refers to the spacial coordinates of all the electrons. $\phi_i(\vec{r})$ are the CSF generated from SOCI. We used the cc-pV5Z basis for all the atomic systems and Roos Augmented Triple Zeta ANO basis for molecular systems [16, 17].

A Jastrow factor is then added to the wave function to correlate electron motion and smooth out the divergence in the local energy near the ions by imposing the cusp condition [18]. Our Jastrow factor contains one and two body terms. The full wave function being optimized is then

$$\Psi_e(\vec{r}) = e^{J(\vec{r}, \vec{\beta})} \sum_{i=1}^{N_{CSF}} \alpha_i \phi_i(\vec{r}) \tag{2}$$

We optimized the CSF and Jastrow coefficients $\vec{\alpha}, \vec{\beta}$ simultaneously with QMCPACK [19].

C. Electron-Ion Wavefunction

Once a satisfactory electronic wave function has been obtained, we construct the electron-ion wave function using the ansatz we previously investigated [5],

$$\Psi_{ei}(\vec{r}, \vec{R}) = \psi_I(\vec{R})\bar{\psi}_e(\vec{r}, \vec{R}), \tag{3}$$

where $\vec{R}$ includes spatial coordinates of all ions. The ion wave function consists of simple products of Gaussian wave functions over each nuclei pair,

$$\psi_I(\vec{R}) \propto \prod_{i,i<j} e^{-a(|\vec{R}-\vec{R}_j|-b_{ij})^2}, \tag{4}$$

where a is a contraction coefficient for the ion wave function that we optimize for each system and b_{ij} are taken
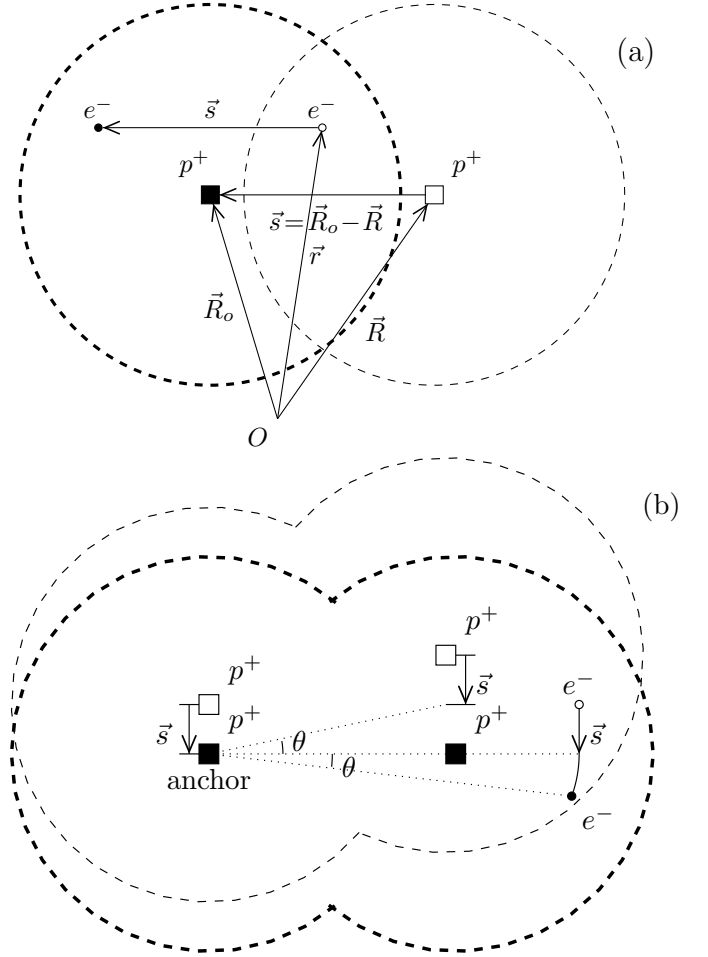

FIG. 1: Dragged node approximation: **(a)** For hydrogen atom, we assume the entire wavefunction shifts with the ion. This process can be visualized by following a contour of the wavefunction. The thick dashed circle represents a contour of the electron wavefunction when the proton is at its reference position $\vec{R}_o$ and the thin dashed circle represents the same contour when the proton has moved to a new position $\vec{R}$. To evaluate the ion-dependent electron wavefunction $\bar{\psi}_e(\vec{r}, \vec{R})$, we simply map the electron to its proper place in the reference wavefunction $\psi_e(\vec{r})$. That is, $\bar{\psi}_e(\vec{r}, \vec{R}) = \bar{\psi}_e(\vec{r}+\vec{s}, \vec{R}_o) = \psi_e(\vec{r}+\vec{s})$ where $\vec{s}$ is the shift required to put the proton back to its reference position. **(b)** For H_2^+, we pick one of the protons as an "anchor" and approximate the new wavefunction by dragging the reference wavefunction with the "anchor" proton. We also rotate the wavefunction to align its axis of symmetry with the orientation of the two protons.

to be the equilibrium distances between the nuclei at the minimum of the potential energy surface of the clamped nuclei. In Fig. 1 we demonstrate this strategy for the simple cases of a hydrogen atom and a H_2^+ molecular ion. Although the dragged-node technique is developed with atomic and diatomic systems in mind, it is not difficult to generalize it for use in larger systems or even apply to parts of a bigger system, e.g., treating light ions as quantum particles and heavy ions as "clamped".

III. RESULTS AND DISCUSSION

A. Ground State Energies

Ground state energies are calculated for first row atoms and ions with and without the adiabatic assumption, see Table I. We first performed a CAS(m,n) calculation (m electrons into n active orbitals) with the ground-state equilibrium geometries taken from experimental data [21]. The MCSCF optimized orbitals are then used in a SOCI calculation that includes single and double excitations of the m electrons into all of the available valance orbitals provided by the basis. We include all CSFs with coefficients bigger than some cutoff ϵ to lend reasonable flexibility to the wavefunction during optimization. We include as many CSFs as possible to maximize the flexibility of the wavefunction. However, the inclusion of too many CSFs with small expansion coefficients can introduces noise as they requires a large number of samples in the optimization step to be optimized. We have chosen to restrict the number of CSFs in the wave function to be ~1000 in all systems. Optimization was performed with roughly 10^7 statistically independent samples and we chose a cost function consisting of equal parts average local energy and reweighted variance. We performed timestep extrapolation for all of the tested systems. Five timesteps from 0.005 Ha^{-1} to 0.001 Ha^{-1} were used for all systems in the adiabatic FN-DMC.

The clamped nuclei ground state FN-DMC energies are consistently equal across all systems, within error bars, with a recent QMC benchmark study [11]. This is an interesting coincidence since we used a different approach in optimizing our wave functions. In particular our large multi-determinant expansions, can be compared with the approach used by Seth *et al.* [11] which used moderately-sized multi-determinant expansions ($\sim$ 100 CSF) with a backflow transformation. For the atomic systems, there are two ECG calculations of non-adiabatic ground state energies we can use as benchmark. The non-adiabatic ground-state energies for Be and B ($-14.66643(2)$ Ha and $-24.65244(3)$ Ha) are in agreement with ECG results to an accuracy of less than 0.2 mHa (-14.66643544 Ha [22] and -24.652598 Ha [23]).

We performed a study over diatomic systems, the results of which are presented in Table II. For these diatomic systems, there are Feller benchmark results [24], for which we can compare our results againsts. To make the comparison against the semi-empirical results, we took the reference energies from the last column of Table VI of Ref. [24] and subtracted the corrections in the ΔE_{SR} and SO columns for comparison with our non-adiabatic energies. For the comparison with our adiabatic energies we subtracted the DBOC and ZPE corrections. Corrections from spin-orbit coupling and relativistic effects are not used, as they are not included in our Hamiltonian.

B. Ionization Energies

The ionization energies are listed in Table I and they agree well with experimental results. Notice that even though ground state energies change significantly with the inclusion of non-adiabatic effects, the ionization energies match with or without the adiabatic assumption. This suggests that for atomic systems, coupling between valence electron and ion motions is small. The difference in ground state energies can be entirely attributed to the zero point motion of the nuclei. Physically, this means that for all first row atoms, the outer most electron is screened from the nucleus and all of the energy required for its removal can be attributed to its interaction with the rest of the electrons in the atom.

For the LiH molecule we are also interested in calculating the electron affinity for comparison to ECG results. We calculated the ground state energy of LiH^- to be $-8.08220(2)$ Ha for the case of clamped nuclei. With non-adiabatic effects included our result is $-8.07811(3)$ Ha. Our non-adiabatic result is in good agreement with a previous ECG study [25] which reported a value of -8.07856887 Ha. We report an electron affinity of $0.01191(4)$ Ha which is can be compared to the ECG prediction of $0.012132(2)$ Ha and agrees with experiment $0.0126(4)$ Ha. We note that LiH ground state energies which we compare against are mislabeled in Ref.[25], with LiH^- and LiD being switched.

C. Atomization Energies

The ground state energies for various hydrides are reported in Table II. The energies calculated for clamped nuclei are on par with the best available quantum chemistry results [26–28]. The energies calculated without the adiabatic assumption are in agreement with the ECG results for LiH, BeH to within 0.4 mHa. In general for small systems, ECG results and typically orders of magnitude more accurate than the best QMC and quantum chemistry simulations. However, with BH being one of the largest ECG simulations performed, the QMC results are actually lower in energy, in this case by 1 mHa. For the systems CH, OH, and HF, there are no explicit simulations we can compare against, and we rely on the experimental results and the results with estimated non-adiabatic corrections for comparison. Our biggest errors appear to occur for BeH and OH. For the case of BeH our agree with accuracy higher than 1 mHa with both the ECG results and semi-empirical benchmarking. In particular the ECG results are converged to more digits than the experimental error bar, and it is likely the experimental reference has errors on the order of 5 mHa. For the case of OH, our error is on the order of 1 mHa, which isn't unexpected as our clamped nuclei ground state energy is roughly 3 mHa from the actual estimated ground state energy.

TABLE I: Ground state energies for atoms and ions, and the ionization energies: Fixed-Node DMC results of this work (FN-DMC) for atoms and ions with and without the adiabatic assumption. The ionization potentials (IP) are reported in the last section of the table with the experimental values. Energies are given in units of Hartree.

Atom	Li(^{2}S)	Be(^{1}S)	B(^{2}P)	C(^{3}P)	N(^{4}S)	O(^{3}P)	F(^{2}P)
			clamped nuclei				
FN-DMC	-7.478056(4)	-14.66732(1)	-24.65377(1)	-37.84449(2)	-54.58858(3)	-75.06576(4)	-99.7316(1)
Seth DMC [11]	-7.478067(5)	-14.667306(7)	-24.65379(3)	-37.84446(6)	-54.58867(8)	-75.0654(1)	-99.7318(1)
Davidson 1993 [20]	-7.47807	-14.66736	-24.65391	-37.8450	-54.5892	-75.0673	-99.7339
			non-adiabatic				
FN-DMC	-7.47742(1)	-14.66643(2)	-24.65244(3)	-37.84277(6)	-54.58655(8)	-75.0631(1)	-99.7290(4)
Ion	Li$^+$(^{1}S)	Be$^+$(^{2}S)	B$^+$(^{1}S)	C$^+$(^{2}P)	N$^+$(^{3}P)	O$^+$(^{4}S)	F$^+$(^{3}P)
			clamped nuclei				
FN-DMC	$-7.279919(4)$	-14.324753(6)	-24.34884(1)	-37.43075(2)	-54.05376(3)	-74.56588(4)	-99.0913(1)
Seth DMC [11]	-7.279914(3)	-14.324761(3)	-24.34887(2)	-37.43073(4)	-54.05383(7)	-74.56662(7)	-99.0911(2)
Davidson 1993[a] [20]	-7.27999	-14.3249	-24.3489	-37.4312	-54.0552	-74.5668	-99.0937
			non-adiabatic				
FN-DMC	-7.2793(1)	-14.32386(2)	-24.34750(3)	-37.42904(4)	-54.05182(9)	-74.56336(8)	-99.0885(3)
			clamped nuclei				
IP (FN-DMC)	0.19814(1)	0.34257(1)	0.30493(1)	0.41374(3)	0.53482(4)	0.49988(5)	0.6403(1)
			non-adiabatic				
IP (FN-DMC)	0.1981(1)	0.34257(3)	0.30494(4)	0.41373(7)	0.5347(1)	0.4997(1)	0.6405(5)
IP (Exp.) [20]	0.19808	0.3425	0.30502	0.413797	0.533967	0.500526	0.640173

[a] The ionic ground state energies are calculated by adding ionization potentials in Table XII to the atomic ground state energies in Table XI from Ref. [20].

TABLE II: Ground state energies and atomization energies: Fixed-Node DMC results of this work for all first row hydrides with and without the adiabatic assumption. Energies are given in units of Hartree.

Molecule	LiH ($^1\Sigma^+$)	BeH ($^2\Sigma^+$)	BH ($^1\Sigma^+$)	CH ($^2\Pi$)	OH ($^2\Pi$)	HF ($^1\Sigma^+$)
			clamped nuclei			
E (this work)	-8.070521(7)	-15.24793(1)	-25.28868(2)	-38.4781(1)	-75.7352(1)	-100.4556(2)
E_{ref} [a] [20, 24, 26–28]	-8.07045	-15.247846	-25.287650	-38.4792(2)	-75.7382(2)	-100.4600(3)
			non-adiabatic			
E (this work)	-8.06620(2)	-15.24196(7)	-25.28103(4)	-38.4704(4)	-75.7237(4)	-100.4445(5)
ECG [22, 23, 25]	-8.0664371(15)	-15.24203(10)	-25.2803(10)	N/A	N/A	N/A
			clamped nuclei			
D_e (this work)	0.092465(8)	0.08062(1)	0.13491(2)	0.13361(2)	0.16944(4)	0.2240(2)
Feller 2008[b] [24]	0.09262(5)	0.0809(4)	0.1354(2)	0.1342(2)	0.1709(2)	0.2258(3)
			non-adiabatic			
D_0^0 (this work)	0.08905(2)	0.07580(7)	0.12886(5)	0.1279(7)	0.1610(4)	0.2158(6)
Feller 2008[c] [24]	0.08940(5)	0.0761(4)	0.1299(2)	0.1276(2)	0.1622(2)	0.2166(3)
Exp. [21]	0.08874(38)	0.0826(11)	0.1281(37)	0.1275(5)	0.1622(1)	0.2158(3)

[a] For the smaller systems (LiH, BeH and BH), ECG studies provide the best reference energies. For CH, OH and HF, we combined the atomic energies in Ref. [20] with the atomization energies in [24] to produce the reference energies.
[b] The non-relativistic atomization energy in the adiabatic limit are calculated by subtracting the scalar relativistic, spin-orbit coupling and zero-point energy corrections from the reference energies in Table VI of Ref. [24].
[c] Here only the scalar relativistic and spin-orbit coupling corrections are subtracted.

IV.   USING MULTIPLE TIME-STEPS

The results of this work given in Tables I and II were obtained from simulations where we moved the nuclei as often as the electrons, i.e., we have used the same time-step for each particle. However, we could also use different sized time-steps for each different particle species as long as they are, e.g., multiples of the smallest time-step. Due to the Trotter expansion [29] this only affects the diffusion term in the diffusion Monte Carlo method, not the branching part. Thus, while applying the kinetic projection operator of the electrons for M times with time-step τ, a heavier particle can use a kinetic projector with time-step $\beta = M\tau$, which is applied only once. Our numerical tests with LiH molecule show that even with $M = 1000$ for the proton, and $M = 4000$ for the Li nucleus the results coincide with those shown in Table II, in which that nuclei were moved as often as the electrons.

However, we believe that for the Li nucleus M could be larger, since in the diffusion term the exponential has a prefactor of $m/2\tau$. Therefore, it is possible that M could be roughly equal to the mass of the particle, since then the prefactor $m/2M\tau$ would roughly be equal to the one found accurate for the electrons.

The major benefit of this "multi-time-stepping" procedure is that going beyond the dragged-node approximation one needs to calculate on-the-fly updates for the electronic wave function each time the nuclei are moved. Thus, the possibility to make external program calls only every thousand steps in case of nonadiabatic hydrogen, and every four thousand (or even ten thousand) steps in case of Li nuclei will enable even more accurate calculations for more complex systems.

V. CONCLUSION

We calculated the ground-state energies of first row atoms and their corresponding ions and hydrides to an accuracy of 0.1 mHa both with and without the adiabatic assumption. We found the ionization energies of the atoms to be independent of the adiabatic assumption, suggesting that the energy difference between the adiabatic and non-adiabatic ground states is due to the zero point motion of the nuclei at the energy scales of interest. The atomization energies of simple hydrides, however, were significantly different in the adiabatic than in the non-adiabatic limit. We showed that it is necessary to include non-adiabatic effects to accurately predict the experimental values of atomization energies for these simple hydrides.

These calculations also verified the validity of our wave function ansatz, namely it does indeed produce a high quality electron-ion trial wavefunction from a good electron wavefunction. This technique also has the potential to solve interesting larger-scale problems due to its ease of implementation as well as the polynomial scaling in computational time with respect to the number of electrons. This technique can be generalized quite easily to deal with larger systems.

VI. ACKNOWLEDGMENT

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