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Spin-orbit interactions in electronic structure quantum Monte Carlo methods

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We develop generalization of the fixed-phase diffusion Monte Carlo method for Hamiltonians which explicitly depends on particle spins such as for spin-orbit interactions. The method is formulated in a zero-variance manner and is similar to the treatment of nonlocal operators in commonly used static-spin calculations. Tests on atomic and molecular systems show that it is very accurate, on par with the fixed-node method. This opens electronic structure quantum Monte Carlo methods to a vast research area of quantum phenomena in which spin-related interactions play an important role.

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I. INTRODUCTION

Quantum Monte Carlo (QMC) methods are making significant contributions to our understanding of many-body effects in quantum systems. Although hampered by the infamous fermion sign problem, a number of approaches have been explored for dealing with inefficiencies whenever sampled distributions possess varying signs or complex values. One of the commonly used strategies is the fixed-node approximation that replaces the fermionic antisymmetry with boundaries given by trial wave function nodes. For broken time-reversal Hamiltonians or for twisted boundary conditions [1] with inherently complex eigenstates, the fixed-node condition has been generalized to the fixed-phase approximation [2]. Benchmark quality results for both models and real materials have been obtained in many settings such as molecules, solids, noncovalently bonded complexes, ultracold condensates and other systems [3,4].

Electronic structure QMC calculations are usually done with particle spins being assigned fixed labels, up or down. Since spins commute with Hamiltonians without explicit spin terms, the problem simplifies to the spatial solution of the stationary Schrödinger equation. Treating the spins as quantum variables for more complicated Hamiltonians was explored very early [5] in variational Monte Carlo (VMC) calculations of nuclear systems. However, extending this to projection methods such as the diffusion Monte Carlo (DMC) in position space [3,4] is much more involved. Building upon results for nuclear systems [6–8], a DMC method has been proposed and applied to a two-dimensional (2D) electron gas with Rashba spin-orbit interaction [9]. In this approach the spinors are stochastically updated by the action of the spin-orbit operator that is absorbed into the path sampling part of the propagator. It effectively samples the space of spinor states rather than (spin) coordinates and a similar VMC approach has been implemented for spin-orbit in atoms [10] very recently.

Here we propose a development that is formulated as the DMC method in coordinate space with spinors in the trial state kept intact during the imaginary time evolution. This implies the zero variance property, i.e., the bias in the obtained energy is proportional to the square of the trial function error.

The method builds upon our previous work [11] on nonlocal pseudopotentials (PP) since the spin-orbit operator is just another case of inherent nonlocality. It is also well suited for calculations of real systems with heavy atoms since both scalar relativistic and spin-orbit effects can be accurately represented by pseudopotentials as is routinely done in quantum chemical calculations [12]. In particular, commonly used semilocal one-particle PP operator $W = \sum_{l,m} v_l(r)|lm\rangle\langle lm|$ is generalized to

$$W = \sum_{l,j} v_{lj}(r) \sum_{m_j} |ljm_j\rangle\langle ljm_j| \tag{1}$$

where $|ljm_j\rangle$ are atomic one-particle spinors, v_{lj} are potential functions, while r is the distance from the ion. The method employs the fixed-phase approximation and therefore depends on the accuracy of the trial function similarly to the fixed-node DMC with static spins.

II. DISCUSSION

A. Phase and absolute value

We assume a Hamiltonian $H = T + V + W$, where V denotes electronic and ionic local interactions while W represents nonlocal and spin-orbit PP terms. Substituting $\Psi = \rho \exp(i\Phi)$ into the imaginary-time Schrödinger equation gives, for the real component,

$$-\partial_t \rho = [T + V + W^{Re} + (\nabla\Phi)^2/2]\rho, \tag{2}$$

where $W^{Re} = \mathrm{Re}[\rho^{-1} \exp(-i\Phi) W \rho \exp(i\Phi)]$. The imaginary component equation describes the phase Φ flow conservation between sources and sinks represented by the imaginary part of W; however, it has no contribution to the total energy since W is Hermitian. In the limit $t \to \infty$, the stationary solution of the real part provides the desired ground-state energy and corresponding ρ.

B. Approximations

In general, neither the exact phase Φ nor W^{Re} are known and we have to introduce approximations. First, we impose the fixed-phase approximation in which Φ is replaced by the trial wave function phase. The corresponding potential is given as

$$(\nabla\Phi)^2/2 \approx (\nabla\Phi_T)^2/2 \tag{3}$$

For a given $V + W^{Re}$ in an ordinary representation it follows that this approximation is variational [2], i.e., the energy expectation with $\rho \exp(i\Phi_T)$ is an upper bound to the exact value for an arbitrary symmetric $\rho \geqslant 0$. Since the fixed-phase solution for ρ is non-negative everywhere by construction, the fermion sign problem is eliminated variationally; this implies the need for accurate approximations to the many-body phase. For the sake of completeness we also note that the fixed-node approximation commonly used in QMC with real wave functions is a special case of the fixed-phase approximation, as had been pointed out by Ortiz *et al.* [2]. In addition, we note that in twist-averaging (Brillouin zone sampling) calculations of periodic systems one employs both fixed-node and fixed-phase approximations on equal footing since they typically exhibit comparable systematic and statistical errors [1].

The second approximation involves the projection of W onto the trial function, similarly to the localization approximation for nonlocal pseudopotentials [11] in spin-free Hamiltonians. W^{Re} is approximated as

$$W^{Re} \approx W_T^{Re} = \mathrm{Re}\big[\Psi_T^{-1} W \Psi_T\big]. \tag{4}$$

This results in a multiplicative many-body operator and one can show that the bias in energy obtained with W_T^{Re} vanishes quadratically in the trial function error [11]. The resulting energy is not necessarily variational; however, the variational property can be recovered with an appropriate modification [13] of the T-moves algorithm [14].

C. Continuous spin and its updates

In its usual representation, the spin configurations have discrete values ±1/2 so that for S_z eigenstates $\chi^{\uparrow}(1/2) = \chi^{\downarrow}(-1/2) = 1$, $\chi^{\downarrow}(1/2) = \chi^{\uparrow}(-1/2) = 0$. The corresponding configuration space is noncompact and therefore would lead to so-called jumps in the evolving stochastic paths. Such jumps could easily make the sampling process rather inefficient since the corresponding local energy fluctuations could go up substantially. Large fluctuations would complicate both the importance sampling and make calculations of larger systems intractable and, eventually, unreachable. Another straightforward option would be to integrate over all spins for every spatial step; however, this would scale exponentially due to the 2^N configurations for N electrons. One way to overcome this difficulty is to introduce a continuous, *overcomplete,* and compact representation [15] that enables us to make the paths smooth. Obviously, we also wish that the spin coordinate space is small so that the sampling can be fast. This points towards the pair of orthogonal states for a one-dimensional (1D) ring as one possible option,

$$\langle s_i|\chi^{\uparrow}\rangle = e^{is_i};\ \langle s_i|\chi^{\downarrow}\rangle = e^{-is_i};\ \langle\chi^{\alpha}|\chi^{\beta}\rangle = 2\pi\delta_{\alpha\beta}. \tag{5}$$

We note that overcompleteness can also compromise the variational property although we estimate that the dominant source of such possible bias would be the localization approximation.

The sampling of spins is done in a manner similar to the spatial degrees of freedom. For this purpose we add spin kinetic energies into the Hamiltonian H for all $s_i, i = 1,\ldots,N$. It includes an effective mass μ_s and an energy offset

$$T_{s_i} = -\frac{1}{2\mu_s}\left[\frac{\partial^2}{\partial s_i^2} + 1\right] \tag{6}$$

so that it annihilates an arbitrary spinor ψ

$$T_{s_i}\psi = T_{s_i}[\alpha\varphi^{\uparrow}(\mathbf{r}_i)\chi^{\uparrow}(s_i) + \beta\varphi^{\downarrow}(\mathbf{r}_i)\chi^{\downarrow}(s_i)] = 0. \tag{7}$$

The offset cancels out the bare spin kinetic contribution; however, T^s does not commute with H so there is some additional contribution to the energy. For the considered strengths of spin orbit, this contribution appears to be small and can be fully eliminated by running the effective spin mass μ_s to zero; this effectively increases the corresponding diffusion constant and in turn speeds up the spin sampling. Another significant effect of such faster spin evolution is that a subset of possible spin configurations gets sampled per single spatial step. This partial averaging statistically approximates the full average over the 2^N space. Since one can adjust the spatial and spin time steps independently, it is possible to carry out extrapolations to find the unbiased values. Due to the fact that the spin functions are very smooth, in the tested cases we found that a spin time step that is 5–10 times larger than the spatial one was sufficient such that the resulting energies were not affected.

D. Importance sampling and trial function

The final step is the importance sampling that is accomplished by multiplying the real part of the Schrodinger equation with the trial function ρ_T. The trial function is a product of the Jastrow factor and Slater determinant(s) of spinors

$$\Psi_T(\mathbf{R},\mathbf{S}) = \exp[U(\mathbf{R})]\sum_k c_k \mathrm{det}_k[\{\psi_n(\mathbf{r}_i,s_i)\}], \tag{8}$$

where $\mathbf{R} = (\mathbf{r}_1,\ldots,\mathbf{r}_N)$ and $\mathbf{S} = (s_1,\ldots,s_N)$. The Jastrow factor includes electron-ion, electron-electron, and possibly higher order terms. Since $U(\mathbf{R})$ depends only on the spatial coordinates, the spin integrations in the nonlocal operator can be done explicitly and the rest is similar to the treatment of nonlocality in static spin calculations [11,13]. The short-time approximation for the importance sampled propagator [3,4] is a product of the dynamical and reweighting factors $G(\mathbf{R},\mathbf{S};\mathbf{R}',\mathbf{S}') = G_{dyn}e^{-\Delta t(E_{loc}+E'_{loc}-2E_T)/2}$, where $E_{loc}(\mathbf{R},\mathbf{S}) = [H\Psi_T]/\Psi_T$. Note that as Ψ_T converges to the exact eigenstate the local energy approaches the exact eigenvalue with vanishing variance pointwise, regardless of the representation or the propagator accuracy. Note that the success of the method depends on the local energies to be mildly varying since large fluctuations could cause very large variance of the exponentials and make the sampling very inefficient. More details about this fixed-phase spin-orbit DMC (FPSODMC) method are further elaborated elsewhere [13].

III. RESULTS

A. Atomic calculations: Excitations in Pb, Bi, and W atoms

We present results for the lowest excitations of Pb, Bi, and W atoms as a testing ground for atomic calculations with spin-orbit effects. This choice is motivated by several considerations. Clearly, the spin-orbit interaction is appreciably large in Pb and Bi. These atoms are often used as the simplest illustrations of the spin-orbit splittings since they exhibit an open shell with only two and three p states, respectively. That makes the splittings at the linear combination of orbitals level analytically transparent and is often used in textbooks [16]. At the same time, the spin orbits in these atoms have impact beyond just finding the corresponding multiplet energies for the well-understood cases. In particular, spin-orbit-induced shift in the ground-state energy changes the key quantities such as energies in chemical bonds by very large amounts, as we illustrate later.

The W atom calculations illustrate another important point. As demonstrated below, the interplay of spin orbit and correlation is needed to find basic properties such as the symmetry and occupation in the ground state of this atom. Note that the effect is significant since these properties are different from its isovalent elements in the same column of the periodic table such as Cr and Mo, despite the fact that Mo exhibits a sizable spin-orbit interaction as well. Therefore, the example of W atom is quite revealing as a demonstration of these combination of effects.

The chosen examples show the introduced method to be on par with essentially the only total energy, wave-function-based alternative, namely, the expansions in Slater determinants with large basis sets. In some cases, the accuracy and agreement between the two approaches enabled us to reveal the accuracy limits of the existing PPs and to point out that a new generation of PPs will be needed in order to harness the full potential of such accurate QMC calculations. Note that the used PPs were constructed in a Dirac-Hartree-Fock formulation, and therefore one does not expect their accuracy to be systematically better than 0.1–0.2 eV for energy differences. Additionally, QMC is scalable to much larger systems. Clearly this positions our method for promising prospects for high-accuracy correlated calculations of larger molecular and solid systems with spin-dependent Hamiltonians.

In the valence-only framework we have tested two types of relativistic PPs for Pb and Bi with spin-orbit terms: large core (LC) with 4 and 5 valence electrons and small core (SC) with 22 and 23 valence electrons respectively [17,18]. The spinors for the Slater determinants are obtained from the two-component Dirac-Fock with complete open-shell configuration interaction (COSCI) calculations using an extensive basis set and the DIRAC13 [19] code. For the COSCI trial wave functions, we include only the local, s, $p_{3/2}$, and $p_{1/2}$ channels in the LC PP, and for the SC we add $d_{5/2}$ and $d_{3/2}$.

We note that unlike in ls coupling the only good quantum number is the total angular momentum J and the lower symmetry is indeed manifested in significant mixing of the states. For example, the ground state $^3P_0(6s^26p^2)$ mixes very strongly with the highest state $^1S_0(6s^26p^2)$ with an amplitude of ≈0.2. Using the same Hamiltonian, we perform a full configuration interaction (FCI) in the two-component formalism to compare with our fixed-phase spin-orbit DMC (FPSODMC) calculations. The total energies from FPSODMC and FCI are shown in Fig. 1. The agreement between the total energies is excellent, showing that as soon as the most significant configurations are included, the fixed-phase approximation shows accuracy that is similar to the conventional static-spin calculations in the fixed-node approximation. The energy differences are listed in Table I and agreement with the experiment is very good, although not perfect, due to small biases in the PP that are visible from essentially perfect agreement between DMC and FCI methods. In addition, we calculate an electron affinity (EA) for the Pb atom that is significantly lower than for other group IVB elements due to the spin-orbit interaction. We find the EA to be 0.417(7) eV that, within the accuracy of the PPs, compares very favorably to the experimental value 0.365(8) eV [21] and also to other theoretical values [22]. In SC calculations the first excited state is closer to experiment than the LC; however, the higher excitations are off by ≈0.2 eV that we assign mostly to the used PP imperfections.

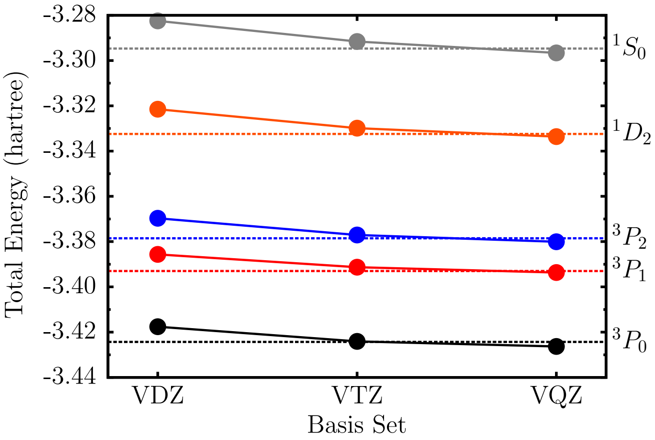

FIG. 1. Total energies of the lowest states of Pb atom from the FCI method (circles) with cc-pVnZ basis sets compared to FPSODMC with a COSCI trial wave function (dashed lines). The valence space includes only 6s and 6p electrons.

For Bi we calculate the first four excitations of the p^3 electronic configuration and for an independent validation we perform CI with single, double, and triple (CISDT) excitations. Results are shown in Fig. 2. The FPSODMC using a COSCI wave function agrees with the total energies for the CISDT to only ≈0.007 hartree. We also test the improvement of the fixed-phase error by including higher excitations into virtual spinors with resulting closer agreement

TABLE I. FPSODMC (DMC for short) excitation energies (eV) of the Pb atom using LC and SC relativistic PPs [17] with COSCI trial function compared with experiment (Exp). For completeness we include also Dirac-Fock COSCI results. The multireference CI (MRCI) and MRCI + core polarization corrections (CPP) calculations [17] are done with the LC PP.

State	COSCI LC	DMC LC	DMC SC	MRCI	MRCI +CPP	Expt. [20]
$^3P_1$	0.83	0.851(1)	0.90(1)	0.90	0.94	0.97
$^3P_2$	1.30	1.245(4)	1.10(1)	1.27	1.32	1.32
$^1D_2$	2.69	2.500(4)	2.42(1)	2.55	2.66	2.66
$^1S_0$	4.06	3.527(5)	3.42(1)	3.54	3.68	3.65

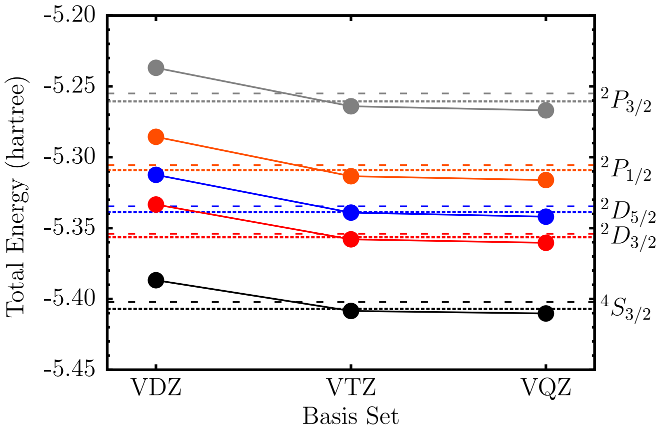

FIG. 2. Total energies of the lowest states of Bi atom from CISDT (circles) with cc-pVnZ basis sets compared to FPSODMC with COSCI (long-dashed lines) and CISDT (short-dashed lines) trial wave functions. The valence space includes only $6s$,$6p$ states.

with the CISDT energies. Although the COSCI is missing some correlation energy (approx. 5–9%) compared to the more extensive FPSODMC-CISDT and CISDT methods, it only adds a constant shift to the spectra since the excitation energies are comparable among all the correlated methods in Table II. We see good agreement for both the LC and SC calculations with the COSCI trial wave function. The FPSODMC with the CISDT trial wave function most accurately reproduces the experimental values.

The next system we calculate is the W atom that shows the importance of both spin-orbit as well as the electron correlation. It is an interesting case since the isovalent Cr and Mo atoms have the ground-state occupations d^5s^1 whereas the ground state of W is d^4s^2. Qualitatively, the d^4 occupation is favored due to the lower energy in the $j = 3/2$ channel; however, it turns out that correlations have to be captured accurately as well. We used a relativistic PP with 14 electrons [23] with two different trial wave functions, COSCI and CISD. The results are listed in Table III. Clearly, the ground state of the Dirac-Fock COSCI method is $5d^56s^1$, indicating that correlation is crucial for correctly calculating the spectrum. Using the CISD as a trial wave function in FPSODMC, we see that not only the states are correctly ordered but also the excitation energies are accurate to within ≈0.1 eV. We note that the FPSODMC-CISD energies are significantly lower than the ones from the basis set extrapolated CISD.

TABLE II. FPSODMC excitation energies (eV) of the Bi atom using LC and SC relativistic PPs [17,18] compared with experiment (Expt.). For completeness we include Dirac-Fock complete open-shell CI (COSCI) and CI (SDT) results. The second row indicates FPSODMC trial wave functions.

State	COSCI LC	DMC-COSCI LC	DMC-COSCI SC	CI LC	DMC-CI LC	Expt. [20]
$^2D_{3/2}$	1.542	1.311(4)	1.38(1)	1.356	1.37(2)	1.415
$^2D_{5/2}$	2.129	1.834(6)	1.74(1)	1.858	1.85(2)	1.914
$^2P_{1/2}$	3.108	2.628(6)	2.53(1)	2.562	2.66(2)	2.685
$^2P_{3/2}$	4.428	4.005(6)	3.95(1)	3.900	3.98(2)	4.040

TABLE III. DMC excitation energies (eV) of the W atom with a relativistic PP [23] compared with CISD and experiment (Expt.). CISD is extrapolated to a complete basis set limit.

Config.	State	COSCI	DMC-COSCI	CISD	DMC-CISD	Expt. [20]
$5d^46s^2$	$^5D_1$	0.098	0.130(9)	0.104	0.15(1)	0.207
$5d^56s^1$	$^7S_3$	−0.845	−0.194(9)	0.115	0.19(1)	0.365
$5d^46s^2$	$^5D_2$	0.244	0.30(1)	0.132	0.30(1)	0.412
$5d^46s^2$	$^5D_3$	0.415	0.49(1)	0.289	0.51(1)	0.598
$5d^46s^2$	$^5D_4$	0.599	0.686(9)	0.452	0.69(1)	0.771

B. Molecular calculations

For the PbO molecule we use the SC PP as recommended [17] so as to avoid overlaps between PPs from the two atoms. The theoretical results of bond length and dissociation energy of PbO molecule together with experimental values are given in Table IV. We also report 1-component CCSD(T) combined with 2-component MRCI studies [17,24] both in PP and all-electron, frozen-core settings. The bond length r_e with the SO interaction shows an excellent agreement with experiment value, compared to an underestimation by ∼0.04 Å in static-spin PP calculations. We also note that the averaged SO treatment overestimates the dissociation energy by ≈0.9 eV whereas we see excellent agreement by explicit treatment of the SO effects.

IV. CONCLUSION

In conclusion, we have proposed a projector QMC method for treating the spins as quantum variables in electronic structure calculations. The method establishes continuous spin coordinate sampling with resulting zero variance algorithm

TABLE IV. PbO bond length (r_e) and dissociation energy (D_e). The DMC calculations are done with the small-core PP and averaged SO represents the fixed-node DMC.

Method	r_e (Å)	D_e (eV)
Spin-free PP-CCSD(T)[a]	1.886	5.14
MRCIS-spss–CCSD(T)[b]	1.923	3.87
Spin-free AE-CCSD(T)[c]	1.937	4.85
SO AE-CCSD(T)[d]	1.934	3.63
DMC, 1-comp. averaged SO	1.88(1)	4.76(3)
FPSODMC, 2-comp.	1.92(1)	3.83(3)
Expt.[e]	1.920	3.87

[a] Spin-free CCSD(T) 1-comp., averaged SO PP [17].

[b] 2-comp. MRCIS with spin-free-state shift evaluated with 1-comp. CCSD(T) [17].

[c] All-electron spin-free CCSD(T) [24].

[d] All-electron SO CCSD(T) [24].

[e] Experimental data [25].

within the fixed-phase approximation and projections of the nonlocal pseudopotentials. The tests on atomic and molecular systems for both total energies and differences show excellent agreement with independent correlated quantum chemical calculations in two-component formalism. The accuracy is very similar to the fixed-node DMC that is widely used for static spins calculations. The method opens QMC to variety of systems across the periodic table such as materials with noncollinear states, spin waves, and other electronic phases for which particle spins are of the key importance.

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