Damped-Core Quantum Monte Carlo Method: Effective Treatment for Large-Z Systems

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A quantum Monte Carlo simulation method is introduced which treats core and valence electrons separately. This greatly minimizes problems associated with the very different energy and time scales present even at a moderate atomic number. The core is treated variationally by Metropolis sampling of a trial wave function, while the chemically important valence region is treated by a quantum Monte Carlo algorithm that solves the Schrödinger equation. We calculate ionization potentials and electron affinities of C, Si, and Ge, and find excellent agreement with experiment. Effective speedup over standard quantum Monte Carlo approaches is estimated to be as large as a factor of 5000.

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In the past several years increasing attention has focused on quantum Monte Carlo (QMC) methods for obtaining atomic, molecular, and chemical properties, including electronic structure.[1-5] QMC is a method of solving the Schrödinger equation stochastically and, with suitable algorithms, exactly. Results obtained have been remarkably accurate and account explicitly for correlation effects. Recently, workers have begun to explore ways that treat only valence electrons,[6-8] motivated by the steep dependence on nuclear charge Z of the computation time required to reduce statistical uncertainties to the level of chemical accuracy. This Z dependence, estimated[7,9] at $Z^{6.5}$, arises partly from the increasingly large fraction of the energy associated with the core relative to the chemically active valence electrons. The core energy rises as Z^2 and, closely related, the time steps that may be taken in the simultaneous decrease as Z^{-2} due to the reduced phase space of the core electrons. This causes extremely poor sampling efficiency for the chemically important valence electrons, while leaving a large "background" energy and variance from the core. Increased sampling efficiency would greatly enhance the speed and broaden the applicability of QMC, a goal being actively pursued.[2,3,6-10] The advantage of treating valence electrons only, for example, with use of pseudopotentials, is that the overall $Z^{6.5}$ dependence weakens to $(Z^{\text{eff}})^{3.4}$, where Z^{eff} is a screened nuclear charge.[7]

The use of pseudopotentials is long established in both solid-state physics and in quantum chemistry for large-scale computations involving heavy atoms. The use of pseudopotentials, however, is known to lead to inaccuracies when core electrons significantly influence the valence electrons through either electronic correlation or polarization effects. Further, every partitioning of core and valence electrons requires computation of a separate pseudopotential, a task requiring additional effort and notably great care.

In this Letter we present a novel approach to the Z-dependence problem that avoids pseudopotentials. We introduce a random-walk QMC method in which the core is treated separately from the valence space, although still by a Monte Carlo method, and valence energies are computed directly. Since most chemical properties derive from the behavior of the valence electrons, we make the approximation that the core may be adequately described by a trial wave function Ψ_{core}. We may, however, choose Ψ_{core} as accurately as desired, even including explicit interelectronic distance terms. Core electrons follow a random walk which distributes them with a probability $|\Psi_{\text{core}}|^2$ by a Metropolis algorithm.[11] The valence electrons are sampled with use of a separate trial function Ψ_{val}. They are, however, treated by a QMC method that "solves" the Schrödinger equation[12] and enables one to sample from the true wave function. From the valence walk, moving in the potential created by the core electrons, one obtains the valence energy of the system.

In this scheme the valence electrons, unrestricted by the much faster core time scale, may take significantly larger steps τ than possible with standard QMC, and rapidly reach equilibrium in the core potential. The core itself also evolves, enabling one to sample a representative distribution of cores. Thus the large-Z dependence is reduced because the valence energy has a much weaker dependence on Z than the total energy, and because time steps appropriate for the valence electrons are readily used. As a result, for a fixed amount of computation, one obtains a much smaller variance.[13] This enables one to treat large-Z atoms to a precision considerably beyond the usual capability of all-electron QMC methods.

The present approach has numerous advantages over pseudopotential methods, though the goals are essentially the same. In fact, in some ways the model potentials used in Ref. 8 are similar: They involve only the Coulomb part of a pseudopotential, and rely on the nodes of the core to generate an excited-state solution for the valence shell. However, unlike the pseudopotentials of any sort, the core electrons are represented explicitly here. Thus, both core polarization and correlation effects may be incorporated systematically, without introducing semiempirical polarization potentials. Further, the separation into core and valence electrons can be defined arbitrarily. Our approach is also more natural within a Monte Carlo framework.

For a system containing N_{core} core electrons and N_{val} valence electrons, the Hamiltonian is separated into

$$H_{\text{core}}=\sum_{s=1}^{N_{\text{core}}}\left[-\frac{1}{2}\nabla_s^2-\sum_A\frac{Z_A}{r_{sA}}+\sum_{t<s}\frac{1}{r_{st}}\right]+V_{NN}-V_{NN}^{\text{val}} \tag{1a}$$

and

$$H_{\text{val}}=\sum_{i=1}^{N_{\text{val}}}\left[-\frac{1}{2}\nabla_i^2-\sum_A\frac{Z_A}{r_{iA}}+\sum_{j<i}\frac{1}{r_{ij}}+\sum_{s}^{N_{\text{core}}}\frac{1}{r_{is}}\right]+V_{NN}^{\text{val}}, \tag{1b}$$

where V_{NN} is the nuclear potential energy and V_{NN}^{val} is taken to be

$$\sum_A\sum_{B<A} Z_A^{\text{eff}}Z_B^{\text{eff}}/R_{AB},$$

with $Z^{\text{eff}}=Z-N_{\text{core}}$. The indices s and t refer to core electrons, i and j to valence electrons, and A and B to nuclei. Atomic units are used throughout.

Generally, a Green's function is used to generate a branching ensemble of configurations that samples the exact wave function.[1] We follow this approach for the valence walk with a modified Green's function G to properly match to the core solution. Specifically, by damping the branching near atomic centers, a smooth crossover is effected from the exact QMC valence walk to the Metropolis walk at the core. This Green's function has the form[14]

$$G(\mathbf{R}\rightarrow\mathbf{R}',\tau)=G_D[G_B]^{\gamma(\mathbf{R})}, \tag{2a}$$

with the damping function given by

$$\gamma(\mathbf{R})\equiv\prod_A\prod_i\{1+\exp[-(r_{iA}-\rho_A)/\alpha_A]\}^{-1}. \tag{2b}$$

The diffusion Green's function is[12,14]

$$G_D=(4\pi D\tau)^{-3N/2}\exp\{-[\mathbf{R}'-\mathbf{R}-D\tau F_Q(\mathbf{R})]^2/4D\tau\}, \tag{3a}$$

while the branching factor is

$$G_B=\exp(-\tau\{[E_L(\mathbf{R})+E_L(\mathbf{R}')]/2-E_T\}). \tag{3b}$$

The functions E_L and F_Q are simply related to the trial wave function.[12] In Eq. (2b), the products are over atomic cores and electrons, respectively, while the parameters ρ and α are a cutoff radius and width. As a valence electron approaches within ρ of an atomic core, $\gamma(\mathbf{R})$ rapidly approaches zero, thereby damping out the branching. Such a walk is precisely our Metropolis QMC walk,[15] yielding the variational distribution $|\Psi_{\text{val}}|^2$ in the core region. Since by construction Ψ_{val} is orthogonal to Ψ_{core}, this prevents the valence solution from "collapsing" into the core.

For the core, we follow a single configuration's random walk rather than an ensemble. This is justified since the core walk is nonbranching, and because ensemble averaging may be replaced by time averaging. Further, a single core walker is advantageous for systems containing a large number of core electrons so that the core evaluation remains a small portion of the total calculation. Each member of the valence ensemble uses the single core configuration for the core-valence two-electron potential (see Fig. 1). Because the core electrons are represented explicitly, some core-valence electronic correlation effects are taken into account. Moreover, core-core electron correlation may be included by use of correlation functions or multideterminant core trial wave functions. Further, because the trial wave function is obtained from an all-electron calculation, the atomic cores are polarized by (and in turn polarize) the molecular environment to the extent of the method used to generate the core trial wave function. Finally, where relativistic effects cause core contraction, a relativistic Hartree-Fock Ψ_{core} used in damped-core QMC will reflect these effects. Such a choice of Ψ_{core} serves the same purpose as the use of a relativistic effective-core potential in QMC.[6]

Although we include core-valence electron correlation through r_{is}^{-1} terms in Eq. (1b), the core configuration

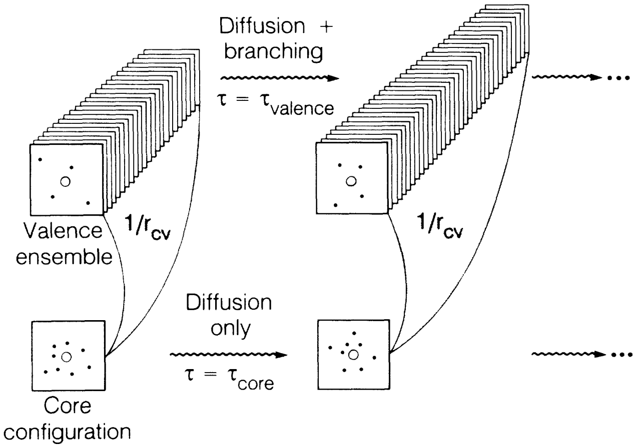

FIG. 1. Schematic diagram of damped-core QMC. The valence ensemble is represented by a stack of configurations. The core ensemble contains only one configuration. Valence electrons interact with the core through the Coulomb potential. Since core electrons are represented explicitly, some core-valence correlation effects are taken into account. Valence configurations evolve by diffusion and branching, moving with a time step τ_{val}, and guided by the trial function Ψ_{val}. The core configuration *only* diffuses, guided by Ψ_{core}, and with a time step τ_{core}.

TABLE I. Ionization potentials of C, Si, and Ge. Uncertainties in the last decimal place are given in parentheses.

Atom	Ionization potentials (eV) Damped-core QMC	Experiment[a]
C	11.2(2)	11.26
Si	8.3(2)	8.15
Ge	8.0(3)	7.90

[a] Reference 18.

TABLE II. Electron affinities of C, Si, and Ge. Uncertainties in parentheses.

Atom	Electron affinities (eV) Damped-core QMC	Experiment[a]
C	1.2(2)	1.27
Si	1.3(2)	1.39
Ge	1.3(3)	1.2(1)

[a] Reference 19.

nevertheless remains unaffected by the valence electrons because the core Hamiltonian and trial wave function were chosen to contain no valence terms. Additional core-valence correlation may be included through use of a multiplicative core-valence correlation function in Ψ_{core}. Also, one need not factor the trial function as done here. Instead, one could use a full all-electron function as Ψ_{val}, fixing the core coordinates at any time step from the separate core walk. An advantage of the latter approach is that one accounts fully for core-valence antisymmetry. However, since the nodes[16] of Ψ_{core} depend only on the core configuration, while the nodes of Ψ_{val} depend on both the valence *and* the core configurations, core moves may result in a valence node approaching a valence walker *without any walker feeling the influence of that node.* This partly reduces the effectiveness of importance sampling, thereby increasing the variance. In the usual all-electron walk the core electrons would be repelled from this node. Our factorization of the trial wave function avoids this problem.

We have implemented the procedure described here and performed damped-core calculations on C, Si, and Ge. Our core and valence trial wave functions were obtained by performing all-electron self-consistent-field calculations (as is commonly done in standard QMC), and using the corresponding molecular orbitals to form the necessary Slater determinants. The atomic double-zeta basis of Clementi[17] were used. Finally, the determinants were multiplied by electron-electron and electron-nuclear correlation functions chosen to satisfy the electron-electron and electron-nuclear cusp conditions.[2,12] The valence ensembles were chosen to have from 100 to 400 members.

Our calculated ionization potentials and electron affinities (cf. Tables I and II), show very good agreement with experiment. The quoted errors should not be considered the limits achievable by this method, since investigation of trial wave functions and computation time for these systems was not exhaustive. Results were found to be fairly insensitive to the choice of the parameters ρ and α. Thus we set ρ to a nominal value from zero to 0.1 a.u. with $\alpha = 0.025$ a.u.

Table III presents data from representative runs on C, Si, and Ge for roughly equal computation times. By comparing valence and core energies and uncertainties the performance of our method can be ascertained. The most striking result is that for each atom the statistical uncertainty of the valence energy is considerably smaller than that of the core, and hence is reduced significantly relative to usual all-electron QMC. This is especially noticeable for Si and Ge. This smaller uncertainty is partly due to the larger valence ensemble, but primarily we obtain greater efficiency because we use time steps up to 3 orders of magnitude larger than possible in usual QMC. For example, the smallest core time step used here was 0.01 a.u. A standard QMC calculation[2] for F required time steps as small as 0.0005 a.u. Scaling by Z^{-2} implies that a similar calculation of Ge would require a time step of about 0.00004 a.u. Thus here the core is being moved faster by a factor of 250. This is possible because the Metropolis sampling has no time-step error. The valence (accounting for most of the computational effort) moves faster still—500 times faster in the present calculation. This ratio is consistent with the ratio of the core to total energies. This speedup derives from the decoupling of the valence from the core, allowing a more natural valence time step to be used. Additional time savings result from the smaller number of active electrons in the wave-function evaluation, and 1 order of Z lower cost in evaluating the Coulomb potential. Overall, for Ge we estimate a speedup of 5000 over standard QMC.

We note that it is also possible to use the same core

TABLE III. Damped-core QMC energies and parameters for C, Si, and Ge, for equal computation times. Quantities are in atomic units. N is the number of electrons, E is the energy, and r is the rms radius obtained in the simulations.

	Carbon	Silicon	Germanium
N_{val}	4	4	4
N_{core}	2	10	28
E_{val}	−5.397(2)	−3.815(7)	−3.798(27)
E_{core}	−32.418(10)	−285.2(5)	−2070.(8)
r_{val}	1.95(1)	2.77(3)	2.88(8)
r_{core}	0.312(8)	0.547(14)	0.598(26)

configurations for the valence walks of the atom and the ion, or more generally for atoms and molecules. In this way additional variance reduction may be achieved through correlated sampling.[1,20] We are currently exploring this approach.

For systems containing very large-Z atoms, a hybrid between pseudopotentials and damped-core QMC can be constructed. For example, for first-row transition metals it is common practice to include the $3s$ and $3p$ shells in the valence space because of their strong overlap with the $3d$ orbitals. In a hybrid approach one could represent the $1s$, $2s$, and $2p$ electrons using pseudopotentials, while using damped-core QMC on the remainder. Only the $4s$ and $3d$ electrons need be in the branching QMC walk. Damped-core and pseudopotential approaches are thus complementary. As discussed earlier, however, the damped-core approach avoids many of the drawbacks of pseudopotentials.

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[13] As implemented with the short-time Green's function of Ref. 12, we find that the damped-core procedure also greatly reduces the time-step bias.

[14] G_D and G_B are the diffusion and branching factors most commonly used in diffusion QMC (Ref. 12). Use of these Green's functions constitutes a short-time approximation accurate to $O(\tau)$. Other Green's functions provide accuracy to $O(\tau^2)$, as in S. M. Rothstein, N. Patil, and J. Vrbik, J. Comput. Chem. **8**, 412 (1987). Exact Green's function Monte Carlo methods are also available. See, e.g., D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics,* edited by K. Binder (Springer-Verlag, Berlin, 1979); and D. M. Ceperley and B. J. Alder, J. Chem. Phys. **81**, 5833 (1984).

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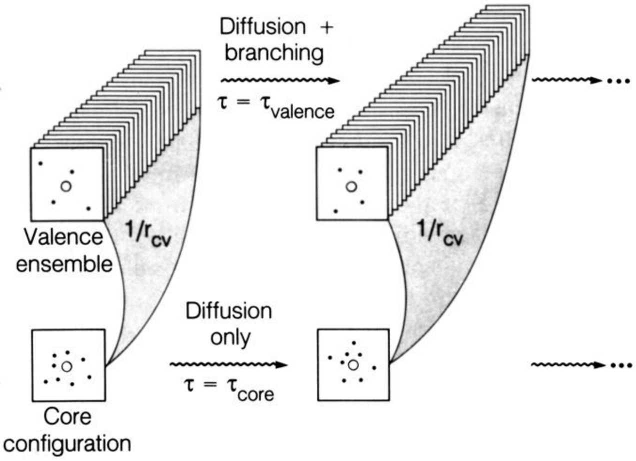

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