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Quantum diffusion computations of two-electron ground-state energies

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A quantum Monte Carlo technique to compute ground-state energies of He, H^-, and Ps^- is described. Coordinates appropriate to a molecular description of atoms are used, and results with good accuracy are obtained upon input of essentially just reduced masses and the nuclear charge. The method minimizes the need to construct sophisticated variational or basis functions.

The dynamics of a pair of electrons moving near an ionic core embodies all the characteristics of the many-body Coulomb problem while minimizing other complicating effects. An advantage of a theoretical study of two-electron atoms is the variety of precision experiments performed over a wide range of energies. Two-electron correlations remain of fundamental interest since a proper description of the pair requires an extreme departure from the notion of independent electrons moving in Bohr orbits.

Variational and close-coupling methods are familiar in atomic and molecular physics for computing stationary states of the time-independent Schrödinger equation. For low-lying levels in two-electron atoms their precision is unsurpassed. A major shortcoming emerges, however, when one considers excitations of two electrons near the threshold for double escape. A successful explanation of experimental observations in this energy range based on variational or close-coupling schemes has never been found. Only limited descriptions exist, such as the Wannier one derived from an expansion of the system wave function about a limited region of configuration space.[1-3] In the conventional methods trial or basis functions must be constructed for each system under consideration and for each energy range. Expansion lengths and convergence must be evaluated on a case-by-case basis. A striking example is the difficulty conventional methods have explaining the remarkable similarities in He, H^-, and Ps^- that the methods themselves so precisely predict. Related techniques such as *adiabatic* hyperspherical-coordinate methods have been found to improve the extraction of physical mechanisms, although high precision is generally difficult to achieve.[1] One is thus inclined to try an alternative solution capable of recognizing the correspondences between these systems but nevertheless one with potential for high accuracy.

An unusual technique that has found good success in computing ground states and some low-lying levels of certain molecules and atoms is the solution of the time-dependent Schrödinger equation as a diffusion equation, that is, as a function of the complex time $\tau \equiv it$.[4-7] In principle, exact eigenfunctions and energies can be obtained from the exponential decay or "diffusion filtering" of an initial or trial function. Consider the formal time development of a solution $\psi(\tau)$ of the diffusion equation $\partial\psi/\partial\tau = -H\psi$, where H is a system Hamiltonian. It is easy to verify that

$$\psi(\tau) = \exp(-H\tau)\phi \;, \tag{1}$$

with ϕ the initial state. This solution can in turn be formally expanded in the desired eigenfunctions χ_n of H as

$$\psi(\tau) = \sum_n e^{-\epsilon_n\tau}\chi_n\langle\chi_n|\phi\rangle \;. \tag{2}$$

Such an expansion makes clear the nature of the diffusion filtering. If $\langle\chi_0|\phi\rangle \neq 0$, the different terms $\exp[-(\epsilon_n - \epsilon_0)\tau]\chi_n$ "filter out" each in turn, like different species in a radioactive sample, leaving as $\tau \rightarrow \infty$ the *exact* ground-state wave function χ_0 when $(\epsilon_1 - \epsilon_0)\tau \gg 1$. In particular, the quantity

$$\epsilon(\tau) = \frac{\langle\phi|H|\psi(\tau)\rangle}{\langle\phi|\psi(\tau)\rangle} \tag{3a}$$

$$\underset{\tau\rightarrow\infty}{\sim} \epsilon_0 + \Delta\epsilon_1 |\langle\chi_1|\phi\rangle/\langle\chi_0|\phi\rangle|^2 e^{-\Delta\epsilon_1\tau} + \cdots \;, \tag{3b}$$

with $\Delta\epsilon_1 = \epsilon_1 - \epsilon_0$, gives the exact ground-state energy ϵ_0 as $\tau \rightarrow \infty$. The diffusion filtering will converge on the first excited state χ_1 if the initial state ϕ is orthogonal, by symmetry for example, to the ground state χ_0.

If the initial state ϕ is taken to be a variational function, obtained by minimizing $\epsilon(\tau=0) = \langle\phi|H|\phi\rangle/\langle\phi|\phi\rangle$, then the diffusion is seen to be self-correcting in as much as it leads itself from the variational trial state ϕ to the exact ground state χ_0. Approximations inherent in the more conventional methods are in principle eliminated. Of particular interest here, this self-correcting feature means that the method is well suited for comparing the three systems He, H^-, and Ps^- with high accuracy but with a minimum of input.

The trial function ϕ can instead be used to improve the efficiency and ultimately the accuracy of the diffusion process by introducing a drift, $\mathbf{D} \sim \phi^{-1} \mathrm{grad}\phi$, into the diffusion equation.[5,6] When ϕ is small the drift is large, driving the diffusion away from regions where ϕ is unimportant. Thus ϕ is often referred to as an "importance function." The diffusion equation for $\psi(\tau)$ is transformed to one for $G(\tau) \equiv \phi\psi(\tau)$, and (3a) is rewritten as

$$\epsilon(\tau) = \frac{\int G(\tau)\epsilon_{\mathrm{loc}}\, dV}{\int G(\tau) dV} \ . \tag{4}$$

Here $\epsilon_{\mathrm{loc}} \equiv \phi^{-1} H\phi$ is a local energy[8] and a function of the particle coordinates. The transformation to $G(\tau)$ also replaces the Coulomb potential in the diffusion equation with the local energy and with a proper choice of ϕ effectively removes destabilizing effects of Coulomb singularities from the diffusion process.

Here we report an application of quantum diffusion as an alternative computational tool for probing two-electron correlations in He, H^-, and Ps^-. We feel that the key is to introduce Jacobi relative coordinates of the interelectronic axis $\mathbf{R}$ and of the position $\mathbf{r}$ of the two-electron center of mass relative to the nucleus. These two vectors specify completely the six coordinate degrees of freedom in the center-of-mass system and reflect the symmetries of the saddle in the three-body potential about the point $r=0$.[1,2] These symmetries have been found to characterize the special Wannier excitations near the double ionization threshold. In addition, this saddle and the resemblance of the two-electron-nucleus configuration to the hydrogen molecular ion have led to a molecular description of two-electron atoms that accounts qualitatively for observed similarities in the lowest doubly excited levels in He, H^- and Ps^-.[3] The relative coordinates facilitate an alliance of this molecular description with quantum diffusion. Although we report computations on only ground states of He, H^-, and Ps^-, we have begun to extend our investigations to low-lying levels for which these symmetries appear to be distinct. Analogous calculations have been performed in molecules.[4,9]

For computational purposes it is convenient to perform the time development as a path integral.[10] One expresses the solution G_{n+1} in the $(n+1)$th time step as a volume integral over particle coordinates of an integral kernal times the solution G_n in the nth time step with $G_0 = \phi^2$. For small enough time steps $d\tau$ the kernal is a product of an exponential-growth factor, determined by ϵ_{loc}, and a normal distribution with a mean determined by the drift $\mathbf{D}$. The diffusion can then be thought of as a long random walk in the system coordinate space. A point in the six-dimensional coordinate space becomes a random walker. The computation thus lends itself to Monte Carlo integration but with a twist. The number of walkers is allowed to increase or decrease in the $(n+1)$th time step depending on the value of the exponential-growth factor. This "branching" process greatly increases computational efficiency by zapping walkers that raise the local energy in the nth time step and replicating walkers that lower it. Initially, the walkers are distributed by some suitable means with a probability $G_0 = \phi^2$ and, as this distribution develops in time, are found in the nth time step distributed according to G_n.

It is then a simple matter to obtain a Monte Carlo estimate of the quantity in (4) in the nth time step as a sum over all walkers N_n of each walker's local energy, $\epsilon(n) \cong N_n^{-1} \sum_q \epsilon_{\mathrm{loc}}(q)$. The well-known advantage of this estimate is that its statistical variance depends largely on the number of walkers as $N_n^{-1/2}$, independent of the number of coordinate dimensions.[10] Most of the effort required in computing the algorithm involves the calculation of the drift $\mathbf{D}$ and the local energy and the Gaussian random numbers for the random walk. The drift and the local energy depend in turn only on the importance function ϕ. Thus the variance of the Monte Carlo estimate of the quantity (4) is also dependent on the quality of the importance function, while the calculational work involved is minimized if the importance function is simple enough. Hence a trade-off between computational speed and diffusion efficiency is sought in the choice of ϕ. This diffusion Monte Carlo technique is similar, and in fact formally related, to the Green's function Monte Carlo method,[11,12] which solves directly the time-*independent* Schrödinger equation and thus eliminates systematic errors introduced by a finite time step. Both methods are referred to collectively as "quantum Monte Carlo."

In the three-body center-of-mass system the local energy is expressed (in atomic units) as

$$\epsilon_{\mathrm{loc}}(\mathbf{r},\mathbf{R}) = \phi^{-1}\left(\frac{-\nabla_r^2}{2\mu_{12,3}} + \frac{-\nabla_R^2}{2\mu_{12}}\right)\phi - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{R} \ , \tag{5}$$

with $r_{1,2} = |\mathbf{r} \pm \frac{1}{2}\mathbf{R}|$, and the drift along $\mathbf{R}$ and $\mathbf{r}$ as

$$\mathbf{D}_R = (\mu_{12}\phi)^{-1}\nabla_R\phi, \ \ \mathbf{D}_r = (\mu_{12,3}\phi)^{-1}\nabla_r\phi \ . \tag{6}$$

To change to a different system all that is required is the input of the nuclear charge Z and the reduced masses.[2,3] Here $\mu_{12} = \frac{1}{2}$ is the reduced mass (in a.u.) of the two electrons, and $\mu_{12,3}$ is that of their center of mass relative to the nucleus. In $H^-(Z=1)$ and He$(Z=2)$, $\mu_{12,3} \simeq 2$, and in $Ps^-(Z=1)$, $\mu_{12,3} = \frac{2}{3}$. The finite mass of the nucleus (mass polarization) is included without approximation, and the method would apply equally well to mesomolecules, such as μdt, of interest in muon-catalyzed fusion.

Appropriate to a molecular description we use an importance function of the form $\phi(\mathbf{r},\mathbf{R}) = f(R) \cdot \varphi(\mathbf{r},\mathbf{R})$. In all computations we have taken the two-electron correlation function to be $f(R) = \exp[R/(1+\beta R)]$ with β a constant.[5] In helium we have found that the single configuration, independent-electron form of the "channel" function, $\varphi(\mathbf{r},\mathbf{R}) = \exp[-\zeta(r_1+r_2)]$ with ζ a constant, gives satisfactory results. In H^- this simple function also permits a satisfactory diffusion, although it gives for the initial variational energy $\epsilon(\tau=0)$ a value above the first ionization threshold, that is, H^- unbound for any choice of ζ. This effect is so severe in Ps^-—the second electron is bound by only 0.326 eV relative to Ps—that the diffusion with this simple function fails to converge at all. Instead, one electron is allowed to walk off to infinity (the first ionization threshold) leaving ground state Ps. The sensitive nature of the Coulomb correlations thus forced us to upgrade the channel function in Ps^- to two configurations

$$\varphi(\mathbf{r},\mathbf{R})=e^{-Z_a r_1-Z_b r_2}+e^{-Z_a r_2-Z_b r_1}\ , \tag{7}$$

akin to Chandrasekhar's variational function,[8] although we found it necessary to include in the screening parameters a mild r_1 or r_2 dependence and define $Z_{a,b}(r_{1,2}) \equiv \zeta_{a,b}+\lambda_{a,b}/(1+c_{a,b}r_{1,2})$. In each computation the constants $\zeta_{a,b}$, $\lambda_{a,b}$, $c_{a,b}$, and β were chosen (by hand) to minimize the initial variational energy $\epsilon(\tau=0)$.

Perhaps we could emphasize that the choice of importance function does not affect the asymptotic mean-value estimates of quantum Monte Carlo dynamical quantities, as long as convergence to the desired bound system has been ensured. The choice can, however, significantly reduce statistical variances as well as the computational labor involved. It is in this sense that a change to a different system requires input of essentially just the nuclear charge and the reduced masses when relative coordinates are used.

Table I presents the results of our computations of the ground-state energies of He, H^-, and Ps^- and a comparison with the best variational values.[13,14] Because of Anderson's extensive quantum diffusion work on helium[15] we have concentrated our computing effort on H^- and Ps^-. Thus in helium we restricted the initial number N_0 of walkers to 3000 but used up to 32000 walkers in H^- and Ps^-. Although this number was allowed to vary as time developed, it remained near N_0 reflecting the stability of the diffusion in the presence of the Coulomb correlations. In each case we diffused for several thousand time steps, some tens of a.u. of time, to converge to the ground state. We continued the diffusion 20 to 50 a.u. of time to obtain an average value for the asymptotic energy $\epsilon(\infty)$ which we took as our best estimate of the ground state energy ϵ_0. It is also of interest to compare with the best adiabatic hyperspherical energies for these systems, which provide upper bounds on ϵ_0. One finds in He that $\epsilon_0 < -2.89517$ a.u.,[16] in H^- that $\epsilon_0 < -0.52592$ a.u.,[16] and in Ps^- that $\epsilon_0 < -0.2597$ a.u.[17]

The statistical errors (standard deviations) associated with this procedure are also given in the table. The errors in the initial variational energies $\epsilon(\tau=0)$ reflect the variance in the Monte Carlo estimate of the sum over the local energies of all the random walkers, distributed at $\tau=0$ according to $G_0=\phi^2$. The efficiency of quantum diffusion is evident when comparing our initial variational energies $\epsilon(\tau=0)$ with the asymptotic averages ϵ_0. Although these computations should in principle be repeated for several time step sizes $d\tau$ and extrapolated to *zero* step size, we show only one since systematic differences in our results with the best variational energies are smaller than our statistical errors, limited mostly by our available computer time.

Our computations were performed on a Ridge 32/130 computer comparable in speed and efficiency to a VAX 11/750 with a floating-point accelerator. We have programmed in C to access its array pointers and avoid array indexing as in FORTRAN. This allows us to minimize bookkeeping as the random walkers are zapped and replicated from one time step to the next. In the nth time step a new list is formed of all the walkers and their daughter walkers that have lowered the local energy and thus survived zapping. At the end of the step this new list is swapped for the old list from the previous time step by a simple exchange of array pointers. Although we have optimized our program for a scalar machine, the algorithm is well-suited for vector and parallel processing.

Although we compute the wave function as an ensemble of points in coordinate space distributed according to $G(\infty)=\phi\psi(\infty)$, it is possible to extract the ground-state distribution $\psi(\infty)=\chi_0$.[11] Thus, one can calculate expectation values of any dynamical variable and even overlap matrix elements,[9,10] such as the μ-He sticking amplitude following muon-catalyzed d-t fusion.[12]

We have begun to extend our calculations to a few special excited states where the symmetries, as determined by the molecular description of atoms,[2,3] can be used to ensure that the importance function is orthogonal to the exact ground-state wave function, $\langle\phi|\chi_0\rangle\equiv 0$. Although it is not presently known how to extend quantum Monte Carlo methods to arbitrary excited states, we feel that the limitation is perhaps a technical difficulty, not a fundamental one, that could be overcome as new ideas are introduced

TABLE I. Results of quantum diffusion computations on two-electron systems. Here N_0 is the initial number of random walkers, $d\tau$ the time step size, $\epsilon(\tau=0)$ the initial variational energy, and ϵ_0 our best estimate of the ground state energy (all quantities in a.u.). Calculations with $N_0=32$ K were performed with the importance function from (7). For comparison, the best variational energies and their differences Δ with ϵ_0 in a.u. and in meV are given.

System	N_0	$d\tau$	$\epsilon(\tau=0)$	ϵ_0	Variational	Δ	Δ (meV)
He	3000	0.01	-2.874 ± 0.006	-2.903 ± 0.001	-2.90372^a	0.00072	17
H^-	3000	0.01	-0.495 ± 0.003	-0.527 ± 0.001	-0.52775^a	0.00075	20
	32000	0.01	-0.5250 ± 0.0004	-0.5275 ± 0.0004		0.00025	6.8
Ps^-	32000	0.05	-0.2573 ± 0.0003	-0.2618 ± 0.0003	-0.26200^b	0.0002	5.4

[a] From Ref. 13.

[b] From Ref. 14.

analogous to extensions of variational and close-coupling methods in two-electron atoms to large radial distances.[1] We note in passing that a reformulation of the *scattering* solution of the Schrödinger equation amenable to Monte Carlo techniques has been recently proposed.[18]

In summary, an algorithm has been described for computing Coulomb correlations in two-electron atoms with a minimum of input. The need to construct better variational or basis functions is minimized; rather an importance function is introduced and the burden of the calculation is shifted to the time development of a distribution of random walkers. The self-correcting feature of the distribution of walkers as the diffusion progresses, unique to quantum Monte Carlo, would appear to have unlimited potential in view of current developments in computer technology. Given enough computing resource the method is capable of benchmark computations of wave functions and expectation values.

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