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# The treatment of exchange in path integral simulations via an approximate pseudopotential

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An approximate form that includes the effects of exchange is suggested for the short time propagator used in path integral simulations. The form is inspired physically by the approximation made in Hartree–Fock treatments of atoms and molecules. The approximate propagator is used with *quantitative* accuracy in two systems: an ideal gas of fermions localized in a three-dimensional harmonic well and the triplet state of the sodium dimer.

## INTRODUCTION

The path integral formulation of quantum mechanics has been successfully used to study a wide variety of condensed phase quantum processes.<sup>1</sup> Unfortunately, most of these studies have been limited to systems where either exchange could be ignored or was not present (single degrees of freedom or systems obeying Boltzmann statistics). In particular, the direct simulation of fermionic degrees of freedom has been hindered by the negative weights that occur when exchange paths are sampled; thus, the exact treatment of exchange in a general quantum system obeying Fermi statistics has not been possible (although Ceperley and Jaccuci have been able to calculate the tunneling frequency in low temperature <sup>3</sup>He,<sup>2</sup> where only nuclear exchange was considered). There are, however, a number of independent electron approximations that work rather well in predicting the *qualitative* behavior of chemical systems (e.g., electrons in a metal). In these models, the only effects of exchange are to enforce the Pauli exclusion principle. This suggests that the development of a spin dependent, potential independent electron–electron interaction that mimics the exclusion principle would allow the study of a variety of chemically interesting systems. We are encouraged by the fact that, in one dimension, exchange takes the form of an effective hard

point interaction<sup>3</sup> (paths cannot cross). While this is not true in more than one dimension, we might expect it to be a reasonable approximation in higher dimensions. It is also well known that the properties of weakly degenerate quantum systems can be mimicked with effective interactions.<sup>4</sup> Thus, there is evidence that a pseudopotential approach to exchange is not doomed to failure. In addition, there are many interesting chemical systems where the effects of exchange should primarily involve pairs of electrons and hence, by treating the two particle exchange problem one may hope to be able to study large numbers of electrons. In this paper, we develop what we call a mean field approximation to the exact quantum partition function for fermions. The form of our pseudopotential is inspired by Hartree–Fock treatments of atoms and molecules, where the effects of exchange are nonlocal in space, suggesting that an approximation that is nonlocal in imaginary time may be an adequate representation of exchange.

## MEAN FIELD APPROXIMATION

Consider the short time propagator for two fermions<sup>5</sup> with Hamiltonian  $\mathcal{H} = \mathcal{h}_1 + \mathcal{h}_2 + V_{12}$ , where  $\mathcal{h}_j$  is the free particle Hamiltonian for particle  $j$  and  $V_{12}$  contains all potential energy terms (including external fields):

$$\begin{aligned} \rho(r_1, q_1, r_2, q_2, \epsilon) &\propto \langle r_1 q_1 | e^{-\epsilon \mathcal{H}} | r_2 q_2 \rangle - \langle r_1 q_1 | e^{-\epsilon \mathcal{H}} | q_2 r_2 \rangle \\ &\propto \langle r_1 q_1 | e^{-\epsilon V_{12}/2} e^{-\epsilon(\mathcal{h}_1 + \mathcal{h}_2)} e^{-\epsilon V_{12}/2} | r_2 q_2 \rangle - \langle r_1 q_1 | e^{-\epsilon V_{12}/2} e^{-\epsilon(\mathcal{h}_1 + \mathcal{h}_2)} e^{-\epsilon V_{12}/2} | q_2 r_2 \rangle \\ &\propto e^{-\epsilon[V(r_1, q_1) + V(r_2, q_2)]/2} [\rho_0(r_1, q_1, r_2, q_2, \epsilon) - \rho_0(r_1, q_1, q_2, r_2, \epsilon)], \end{aligned}$$

where  $\rho_0$  is the free particle propagator. As can be seen, in this approximation the effects of exchange reside entirely within the free particle (kinetic energy) terms. In other words, we have hope that the effects of exchange should be potential *independent*, at least within the short time approximation. For the rest of this section, then, we will consider the short time propagator for two noninteracting fermions. This is given by

$$\begin{aligned} \rho(r_1, q_1, r_2, q_2, \epsilon) &\propto \langle r_1 q_1 | e^{-\epsilon(\mathcal{h}_1 + \mathcal{h}_2)} | r_2 q_2 \rangle - \langle r_1 q_1 | e^{-\epsilon(\mathcal{h}_1 + \mathcal{h}_2)} | q_2 r_2 \rangle \propto \left[ \frac{m}{2\pi\epsilon\hbar^2} \right]^3 \left( \exp \left\{ -\frac{m}{2\epsilon\hbar^2} [(r_1 - r_2)^2 + (q_1 - q_2)^2] \right\} \right. \\ &\quad \left. - \exp \left\{ -\frac{m}{2\epsilon\hbar^2} [(r_1 - q_2)^2 + (q_1 - r_2)^2] \right\} \right) \propto \rho_0^B(r_1, q_1, r_2, q_2, \epsilon) \left\{ 1 - \exp \left[ -\frac{m}{\epsilon\hbar^2} (r_1 - q_1) \cdot (r_2 - q_2) \right] \right\}, \end{aligned}$$

where  $r_1$  and  $r_2$  are the coordinates of particle 1,  $q_1$  and  $q_2$  are the coordinates of particle 2,  $m$  is the mass,  $\rho_0^B$  is the free particle propagator for distinguishable particles, and  $(r_1 - q_1) \cdot (r_2 - q_2)$  denotes a dot product. In this form, it is

clear that  $\rho$  can be negative, since the dot product can be less than zero. Thus, in its exact form, the free particle propagator for exchange allows for negative weights and, thus, cannot be used in a Monte Carlo simulation unless umbrella



where  $r$ ,  $q$ , and  $z$  refer to the three quantum particles. As a first guess we might write the term in brackets as

$$[(1 - f_{12}) \cdot (1 - f_{13}) \cdot (1 - f_{23})],$$

i.e., only including the lowest order terms. Such a factorization will work reasonably well at high temperatures when the fermions are fairly localized and for systems in which the fermions have a strong repulsive interaction that prevents the close approach of more than two fermions at a time. At low temperatures, however, it becomes necessary to include the three-body terms. Thus, we write

$$\begin{aligned} & [1 - f_{12} - f_{13} - f_{23} + g_{231} + g_{312}] \\ &= [(1 - f_{12}) \cdot (1 - f_{13}) \cdot (1 - f_{23}) \\ & \quad \cdot (1 + g_{231} - \dots) \cdot (1 + g_{312} - \dots)] \\ & \cong [(1 - f_{12}) \cdot (1 - f_{13}) \cdot (1 - f_{23}) \cdot (1 + 2g_{231}) / \\ & \quad (1 + g_{231}) \cdot (1 + 2g_{312}) / (1 + g_{312})], \end{aligned} \quad (3)$$

where we have approximately summed the infinite series to infinity. This approximate summation is necessary if we wish to include the effects of four and higher body effects for more than three fermions. We then replace all dot products with  $\alpha$  times their absolute value and obtain a nonnegative weight for the path integral calculations. Given these approximate interactions, we now study two model systems: an ideal gas of fermions and the sodium dimer.

#### APPLICATION: HARMONIC OSCILLATOR

We apply the method [using Eq. (3)] to a simple system, a three-dimensional harmonic oscillator. We choose three dimensions in order to avoid any pathologies in one dimension, where we know that a hard-point-like interaction will be exact. As we place more particles into the harmonic well, our interaction should force them to obey the Pauli exclusion principle and go into higher energy levels. We have tested this interaction at four temperatures and for up to five spin up quantum particles. Our simulations have used the sampling method of Ceperley and Pollack<sup>8</sup> as implemented by Coker *et al.*<sup>9</sup> We have adjusted  $\alpha$  to give the correct results for two spin up fermions at a temperature  $\beta\hbar\omega = 3.0$ . The results are shown in Table I, where nearly quantitative accuracy is obtained. The small, systematic deviations for  $N \geq 4$  are due to four- and five-body exchange terms that we are neglecting in our treatment. While these terms will be important for an ideal gas of fermions all localized about a single site (as in this example), it is doubtful that once the electron-electron repulsions are turned on and the number of nuclear sites increases (as in the case of a metal cluster or an amorphous solid) the effects of these higher body exchanges should be significant. For temperatures lower than  $\beta\hbar\omega = 6.0$ , our approximation for three-body interactions breaks down. We can, however, keep more of the exact terms in Eq. (3) and obtain better agreement.<sup>6</sup> This means that we must be careful if we wish to study exchange in many-electron atoms. However, for systems with unbound electrons, we believe our approximation can be used with accuracy.

TABLE I. Energy of an ideal gas of fermions localized in a three-dimensional harmonic oscillator. Temperatures are given in terms of  $\beta\hbar\omega$ ,  $P$  is the number of points in the discretized path integral chain, and  $N$  is the number of spin up fermions.  $E_{MC}$  are the results with the mean field approximation,  $E_q$  is the exact quantum energy,  $E_{Boltz}$  is the energy of a similar number of particles obeying Boltzmann statistics, and  $E_{class}$  is the classical energy. Energies are given in units of  $N\hbar\omega$  and the numbers in parentheses are one standard deviation.

$N$	$E_{class}/N\hbar\omega$	$E_{Boltz}/N\hbar\omega$	$E_q/N\hbar\omega$	$E_{MC}/N\hbar\omega$
$\beta\hbar\omega = 1.5 \quad P = 5$				
2	2.0	2.362	2.595	2.596(0.014)
3	2.0	2.362	2.816	2.817(0.011)
4	2.0	2.362	2.999	2.963(0.010)
5	2.0	2.362	3.153	3.085(0.010)
$\beta\hbar\omega = 3.0 \quad P = 10$				
2	1.0	1.657	2.078	2.078(0.001)
3	1.0	1.657	2.324	2.343(0.005)
4	1.0	1.657	2.498	2.508(0.004)
5	1.0	1.657	2.637	2.612(0.005)
$\beta\hbar\omega = 6.0 \quad P = 20$				
2	0.5	1.507	2.003	2.001(0.003)
3	0.5	1.507	2.178	2.284(0.003)
$\beta\hbar\omega = 60.0 \quad P = 200$				
2	0.05	1.50	2.000	2.004(0.002)

#### APPLICATION: SODIUM DIMER

We now demonstrate that our pseudopotential is potential *independent*. As stated previously, we have hope that the effects of exchange are manifest primarily in the kinetic energy term. To test this, we have used the pseudopotential from the previous section (with  $\alpha = 0.6$ ) to calculate the energies of the sodium dimer in its triplet state. We have used the one electron effective Hamiltonian of Preuss *et al.*<sup>10</sup> to describe the valence electron-atom interaction. Thus, our simulation has two electrons and two ionic cores. We have chosen  $\beta = 120$  a.u., for which excited state effects are negligible. Our results for two different internuclear separations are shown in Table II. Energies are given in atomic units and are listed relative to the value at infinite separation. Also included in the table are the MCSCF results of Konowalow, Rosenkrantz, and Olsen.<sup>11</sup> As can be seen, the Monte Carlo results are in excellent agreement with the MCSCF results and, hence, our pseudopotential is indeed potential independent.

#### CONCLUSIONS

We have developed an effective pseudopotential for treating exchange in many-fermion systems. This potential

TABLE II. Energies for the Na dimer in its triplet state. All numbers are in atomic units and are given relative to their values at infinite separation.  $\beta = 120$  atomic units and  $P = 200$ .  $E_{MC}$  are the energies calculated in the current work and  $E_{MCSCF}$  are the values from Ref. 11. Numbers in parentheses represent one standard deviation.

$R$	$E_{MCSCF}$	$E_{MC}$
6.0	+ 0.010 449 0	+ 0.008(0.004)
4.0	+ 0.066 348 0	+ 0.063(0.004)

has been shown to be temperature and potential independent, suggesting it will be useful in a variety of chemically interesting systems. We believe that this approach will be particularly useful in systems without strongly coupled electronic degrees of freedom, such as conduction electrons. The approximation breaks down under some circumstances, primarily when more than three noninteracting fermions of the same spin are localized about a single site. It will be of some interest to see if this breakdown is important when the electron-electron interactions are turned on, as will be the case in the ground state of a many-electron atom. It is possible that the electron-electron repulsion terms will keep the electrons far enough apart that four- and five-body exchange terms will become unimportant. It will also be important to determine if the mean field-type approximation we have made does not effectively treat correlation between electrons, since, while correlation is included in the exact position representation propagator, it is not necessarily there once we have made the exchange interaction nonlocal. To examine these limitations, it is necessary to study some many-electron atoms where correlation energies are known to be large.

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