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Kink-Based Path Integral Calculations of Atoms He-Ne

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Abstract

An adaptive, kink-based path integral formalism is used to calculate the ground state energies of the atoms He-Ne. The method uses an adaptive scheme to virtually eliminate the sign difficulties. This is done by using a Monte Carlo scheme to identify states that contribute significantly to the canonical partition function and then include them in the wavefunctions to calculate the canonical averages. The calculations use the 6-31G basis set and obtain both precision and accuracy.

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I. INTRODUCTION

The path integral formulation of quantum mechanics offers a variety of advantages for studying the electronic and geometric structures of multi-electron systems[1]. Chief among these are inclusion of finite temperatures (particularly as they affect geometric degrees of freedom) and exact inclusion of electron-electron correlation. The application of this method to electronic systems has been hindered by the so-called "sign" problem, which results from sign of the fermion density matrix, which can be positive or negative and leads to large uncertainties in quantities evaluated using statistical methods such as Monte Carlo simulations[2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19]. We have recently introduced a "kink-based" path integral approach[19], which was demonstrated to overcome the sign problem in the 2-D Hubbard model. This approach is complimentary to the shifted-contour auxiliary-field Monte Carlo method[15, 16, 17, 18], which uses the Hubbard-Stratonovich transformation to combat the sign problem. In this work, we use the kink-based formalism to study atomic systems, the next step in studying systems with geometric degrees of freedom (such as atomic clusters).

II. KINK-BASED APPROACH

In this section, a brief review of the kink-based approach[19] is given, with additional attention given to the different spin states that are encountered in electronic systems. The partition function is written:

$$\begin{aligned} Q &= Tr\{\exp(-\beta H)\} \\ &= \sum_{\sigma,\alpha} \langle \alpha, \sigma | \exp(-\beta H) | \alpha, \sigma \rangle \\ &= \sum_{\sigma,\alpha} \exp(-\beta E_{\alpha,\sigma}) \end{aligned} \tag{1}$$

where α labels the different electronic states associated with a particular spin state σ and $|\alpha, \sigma\rangle$ is the properly anti-symmetrized state. For large enough β , this becomes

$$Q \approx \exp(-\beta E_{0,\sigma^*}) \tag{2}$$

where E_{0,σ^*} is the ground state energy of the lowest energy spin-state. If an approximate set of states, $\{a, s\}$ is used, we have

$$\begin{aligned} Q_{\{a,s\}} &= \sum_{a,s} \langle a, s | \exp(-\beta H) | a, s \rangle \\ &= \sum_{a,s} \sum_{\sigma,\alpha} | \langle a, s | \alpha, \sigma \rangle |^2 \exp(-\beta E_{\alpha,\sigma}) \end{aligned} \quad (3)$$

As long as $\langle a, s | 0, \sigma^* \rangle \neq 0$ for some a and s , then as β gets large,

$$Q_{\{a,s\}} \propto \exp(-\beta E_{0,\sigma^*}) \quad (4)$$

In a later section, we will choose our states with specific values of S_z . Consequently, we will determine the low temperature partition function corresponding to the lowest energy spin-state S that has S_z as one of its possible values of \hat{S}_z .

To evaluate the partition function $Q_{\{a,s\}}$ using the path integral method, we insert complete sets of states in order to use the high temperature, semi-classical approximation for the density matrix:

$$\begin{aligned} Q_{\{a,s\}} &= \sum_{a_1, s_1} \cdots \sum_{a_P, s_P} \langle a_1, s_1 | \exp(-\beta H/P) | a_2, s_2 \rangle \cdots \\ &\quad \times \langle a_P, s_P | \exp(-\beta H/P) | a_1, s_1 \rangle \\ &\equiv \sum_{a_1, s_1} \cdots \sum_{a_P, s_P} t_{a_1, s_1}^{a_2, s_2} \cdots t_{a_P, s_P}^{a_1, s_1} \end{aligned} \quad (5)$$

We refer to a matrix element $\langle a, s | \exp(-\beta H/P) | a', s' \rangle$ with $a \neq a'$ or $s \neq s'$ as a *kink*.

We rewrite the partition function as a sum over kinks:

$$\begin{aligned} Q_{\{a,s\}} &= \sum_{a,s} (t_{a,s}^{a,s})^P + \\ &\quad \sum_{i=1}^P \sum_{a,s} \sum_{a',s'} (t_{a,s}^{a,s})^i (t_{a',s'}^{a',s'})^{P-2+i} (t_{a,s}^{a',s'})^2 + \cdots \end{aligned} \quad (6)$$

$$\equiv Q_0 + Q_2 + Q_3 + \cdots + Q_P \quad (7)$$

where Q_n is the partition function corresponding to n kinks. In our previous work, we demonstrated that $Q_{\{a,s\}}$ has the form

$$\begin{aligned} Q_{\{a,s\}} &= \sum_j x_j^P + \\ &\quad \sum_{n=2}^P \frac{P}{n} \left(\prod_{i=1}^n \sum_{j_i} \right) \left(\prod_{k=1}^n t_{j_k, j_{k+1}} \right) S(\{x_j\}, n, m, \{g_j\}) \end{aligned} \quad (8)$$

where

$$x_j = \langle \alpha_j, s_j | \exp(-\beta H/P) | \alpha_j, s_j \rangle \approx \langle \alpha_j, s_j | (1 - \beta H/P) | \alpha_j, s_j \rangle$$

$$t_{j,j'} = \langle \alpha_j, s_j | \exp(-\beta H/P) | \alpha_{j'}, s_{j'} \rangle \approx \langle \alpha_j, s_j | (1 - \beta H/P) | \alpha_{j'}, s_{j'} \rangle$$

and $S(\{x_j\}, n, m, \{g_j\})$ is the contribution to the partition function with n kinks, comprised of m states α_j , each occurring g_j times ($\sum_j g_j = P - n$). The explicit form for S is

$$S(\{x_j\}, n, m, \{g_j\}) = \sum_{l=0}^m \frac{1}{(g_l - 1)!} \frac{d^{g_l-1}}{dx_l^{g_l-1}} \frac{x_l^{P-1}}{\prod_{k \neq l} (x_l - x_k)^{g_k}} \quad (9)$$

The derivatives can be evaluated recursively. If we define

$$F_l^{(p)} \equiv \frac{d^p}{dx_l^p} \frac{x_l^{P-1}}{\prod_{k \neq l} (x_l - x_k)^{g_k}} \quad (10)$$

we can show

$$S = \sum_{l=1}^m \frac{F_l^{(g_l-1)}}{(g_l - 1)!} \quad (11)$$

$$F_l^{(n)} = \sum_{m=0}^{n-1} \binom{n-1}{m} G_l^{(m)} F_l^{(n-1-m)} \quad (12)$$

$$G_l^{(m)} = (-1)^m m! \left[\frac{P-1}{x_l^{m+1}} - \sum_{k \neq l} \frac{g_k}{(x_l - x_k)^{m+1}} \right] \quad (13)$$

$$(14)$$

A similar manipulation leads to an expression for the energy estimator:

$$E_{est} = \sum_{i=1}^n \frac{t'_{i,i+1}}{t_{i,i+1}} + \frac{1}{S} \sum_{l=0}^m \frac{1}{(g_l - 1)!} \sum_{j=0}^{g_l-2} \binom{g_l-2}{j} \left[D_l^{(j)} F_l^{(g_l-2-j)} + G_l^{(j)} E_l^{(g_l-2-j)} \right] \quad (15)$$

$$E_l^{(m)} \equiv -\frac{d}{d\beta} F_l^{(m)} \quad (16)$$

$$D_l^{(m)} \equiv -\frac{d}{d\beta} G_l^{(m)} \quad (17)$$

The expression shown in Eqn. 9 gives the exact value of Q (including electron-electron correlation) within the approximations inherent in using a finite basis set and a finite level of discretization. The so-called "sign problem" can occur in this and any other discretized

version of the path integral problem because any of the matrix elements $t_{i,i+1}$ can be negative, resulting in a large variances when evaluating the partition function using simulation methods. Our approach to minimizing or eliminating the sign problem has been to apply Eqn. 9 in an adaptive manner. We first realize that the zero kink contribution to Q has no sign problems, since the system is in a single state. With a properly chosen states, Q can be obtained with just a few kinks; this significantly reduces the sign problem by reducing the statistical error from greater than 100% to a precision adequate for chemical applications. A good choice for the states is obtained using a Monte Carlo simulation, in which the different N -electron states that appear during the simulation are used to update the estimates of the ground and excited states. We call this approach an adaptive approach, since the Monte Carlo algorithm allows the estimates for the ground and excited state wavefunctions to evolve according to the statistical sampling of the different N -electron states.

We implemented the adaptive scheme in the following way (other methods of are possible). An initial set of basis functions (the 6-31G basis set in our calculations) was orthonormalized and used to create a set of one-electron orbitals. The one-electron Hamiltonian was then diagonalized in this basis. Each electron was assigned a spin and the one-electron basis functions were combined to form a set of Slater determinants (as described earlier, the lowest energy spin state will be projected out by the path integral procedure) that were then used as the initial $|\alpha, s\rangle$ for the Monte Carlo simulation. A simulation using the absolute value of the summand in Eqn. 9 as the weighting function was performed in which kinks were added, removed, and changed. An upper limit on the number of kinks allowed was set to 10 kinks; since the final results were obtained with 0 or 2 kinks, this did not affect the accuracy of our results. A list of the states accepted was kept. If the fraction of configurations that contained more than 0 kinks was greater than the fraction of configurations that had 0 kinks, the Hamiltonian was diagonalized using the current list of states and a new set of N -electron states obtained. These new diagonalized states were linear combinations of the initial set of Slater orbitals and thus corresponded to configuration interaction (CI) wavefunctions. Since the simulation sums over all possible states, in essence a complete CI calculation is performed. Another possible Monte Carlo scheme would allow the individual Slater determinants to be altered during the simulation, which would correspond to a MC-SCF calculation. At most 100 states were included in the diagonalization to limit the time per diagonalization. If the set of accepted states exceeded 100 at the time of diagonalization,

only the 100 most prevalent states were included. Once 5000 iterations had occurred with no diagonalizations, the run was terminated and these final 5000 energies used to determine energies. At the end of the calculation, the ground state would correspond to a high quality CI ground state; if the state does not correspond to the complete CI wavefunction, then kinks will be added to correct the ground state. If the adaptive procedure provides the complete CI wavefunction, then no kinks would ever be introduced, as the density matrix would be diagonal. In practical calculations, we expect to stop the adaptive process before the density matrix is actually diagonal, but when the off-diagonal matrix elements are so small that the likelihood of adding more than 2 kinks is very small. In fact, in our calculations, the Monte Carlo procedure provided such a good estimate of the true ground state that at any time we found only 0 kinks or 2 kinks (to one of the excited states).

III. APPLICATION TO ATOMIC ENERGIES

We have tested this approach by applying it to atomic systems, using the 6-31G basis set. This set was chosen for its relative simplicity and reasonable accuracy. For each atom, He-Ne, each electron was assigned a specific s_z , leading to a fixed total S_z . Thus, the sum in Eqn. 5 used just a single spin state which was a linear combination of states S such that S_z was one of the possible values of \hat{S}_z . The initial basis functions were orthonormalized and the one-particle Hamiltonian was diagonalized, providing an initial set of states. As the Monte Carlo simulation was performed and diagonalizations proceeded as previously described. Our results are shown in Table I, along with the Hartree-Fock and CASSCF energies from Gaussian 98[20]. The average sign of the density matrix demonstrates that the adaptive approach adequately reduces sign problem to well below what is needed for chemical accuracy. For comparison, we note that a shifted-contour auxiliary-field Monte Carlo calculation of Ne[16], using a 4-31G basis set, led to errors of 0.004 a.u., significantly larger than those found in the present calculations. For illustrative purposes, Table II shows the evolution of the coefficients of the Slater determinants that contribute significantly to the ground state wavefunction of Be, during the first 4 updates. After the first 4 updates, only minor changes occurred in the ground state. It can be seen that the adaptive procedure introduces mixing between the Slater determinants as needed. The degeneracies seen can be rationalized on the basis of symmetry.

Atom	E(HF)	E(CASSCF)	E(MC, P= 10^{13})	$\langle Sign \rangle$	N_{up}	N_{down}
He	-2.855160	-2.8701621	-2.8701621(0)	1.0000(0)	1	1
Li	-7.4312350	-7.4315542	-7.4315535(6)	1.0000(0)	2	1
Be	-14.5667641	-14.6135453	-14.6135468(22)	1.0000(0)	2	2
B	-24.5193448	-24.5628917	-24.5628918(14)	1.0000(0)	3	2
C	-37.6768656	-37.7162644	-37.7162663(24)	1.0000(0)	4	2
N	-54.3820508	-54.4199396	-54.4199404(32)	1.0000(0)	5	2
O	-74.7782342	-74.8394081	-74.8394091(38)	0.9992(11)	5	3
F	-99.3602182	-99.4474231	-99.4474225(34)	0.9996(8)	5	4
Ne	-128.4738769	-128.5898023	-128.5898026(24)	0.9996(8)	5	5

TABLE I: Hartree-Fock (HF), CASSCF, and path integral (MC) energies (in atomic units), and average sign of the density matrix for the different atoms studied in this work. The numbers in parenthesis represent 2 standard deviations. The number of up- and down-spin electrons is also specified.

Update Number	E(ground state)	State 1	State 2	State 3	State 4	State 5
	Degeneracy	1	2	1	3	6
1	-14.3543	1.0	0.0	0.0	0.0	0.0
2	-14.6053	0.7788	-0.3729	0.1408	-0.1340	-.07652
3	-14.6131	0.7782	-0.3726	0.1407	-0.1339	-.07645
4	-14.6135	0.7715	-0.3767	0.1452	-0.1343	-.07872

TABLE II: Energies (in atomic units) and coefficients of the ground state wavefunction, as a function of adaptive update, for the first 4 adaptive updates of Be. States are arbitrarily labeled and correspond to multiple states with degeneracies as indicated. The Monte Carlo procedure identified all degenerate states and mixed them with identical coefficients.

IV. CONCLUSIONS

The adaptive, kink-based approach to path integral calculations has been applied to atomic systems. As was the case in our previous work, the use of the adaptive approach reduced the sign problem to a tolerable level. While we have used an adaptive diagonalization

procedure to improve our estimates for the electronic states, this is not an essential ingredient in the adaptive approach. For instance, unitary transformations can be sampled as part of the Monte Carlo process. In addition, we have not made any simplifying assumptions that will be required when treating systems with large numbers of basis functions, such as limiting the type of determinant that can contribute to the ground state wavefunction. We note that the number of electrons and basis functions used in this study is on the order of that needed to study moderately large metal clusters. For example, Na_{20} would require roughly 10 shell-orbitals (orbitals centered at the origin of the cluster, in accord with the shell model of the electronic structure) and 20 electrons, if pseudopotentials are used for the core electrons. Thus, the current method may be applicable to moderately large systems.

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