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COMMUNICATIONS

Adiabatic diffusion Monte Carlo approaches for studies of ground and excited state properties of van der Waals complexes

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Several adiabatic extensions to the diffusion Monte Carlo approach are presented. In the first, an adiabatic form of the finite field method is developed for the systematic evaluation of expectation values. In addition, an adiabatic flexible node method for calculating excited states is described. The above methods are applied to NeSH and Ar_2HCl where comparisons to results of variational calculations can be made. © *1999 American Institute of Physics.* [S0021-9606(99)02712-9]

I. INTRODUCTION

The diffusion Monte Carlo (DMC) approach, initially proposed by Anderson,[1] has developed into a very powerful technique for studying low-lying vibrational states of weakly bound complexes.[2] The advantage of this approach comes in its generality and its favorable scaling with the size of the system. The basis of DMC comes from the identical structures of the diffusion equation and the time-dependent Schrödinger equation, when it is written in terms of $\tau = it$. In DMC, an ensemble of several thousand replicas, called walkers, are allowed to diffuse in the configuration space of the system of interest, with the masses providing the diffusion constants and the potential energy adding a source/sink term.[1,3] At long τ, the distribution of configurations represents the ground state wave function and the ground state energy E_0 is obtained by the requirement that the number of walkers is approximately constant. Typically E_0 can be calculated with a 1% uncertainty. While this is not as accurate as variational treatments, the DMC approach is general and can be easily applied from complexes consisting of two or more weakly bound species without significant modifications to the algorithm.

There are several potential drawbacks of the DMC approach. First, because the calculated E_0 contains statistical uncertainty, it is advantageous to remove the contributions to E_0 from the high frequency intramolecular vibrations in studies of the spectroscopy and dynamics of the weak intermolecular interactions in van der Waals complexes. Buch has proposed a rigid body formulation of DMC (RBDMC) that treats only the translational and rotational motions of the molecular units in the complex.[4] Even within the RBDMC framework, the wave function is given as a distribution of thousands of replicas, making the direct calculation of properties other than the energy, non trivial. In addition, because DMC is a relaxation method, it can only be directly applied to states for which one already knows the location of the nodes, for example the lowest energy state of a particular symmetry. In this communication, we will present our solutions to these two problems, and will compare the results of RBDMC simulations for NeSH and Ar_2HCl to those obtained from calculations based on the variational principle.[5,6]

II. ADIABATIC DIFFUSION MONTE CARLO (ADMC)

One of the severe disadvantages of DMC approaches comes from the fact that the distributions that are obtained from a random walk represent the wave function, rather than $|\psi|^2$. As such, there is no way to directly calculate properties of the system other than the energy by DMC. Several approaches have been suggested for evaluating expectation values from DMC runs.[3,7] One promising approach uses a finite field scheme[8] that is similar to the one used in electronic structure calculations to evaluate electric and magnetic properties of molecules.[9]

In the finite field approach, one takes advantage of the result of first order perturbation theory that if

$$\hat{H} = \hat{H}^{(0)} + \lambda W, \tag{1}$$

then $E_n(\lambda) = E_n^{(0)} + \lambda \langle \psi_n^{(0)} | W | \psi_0^{(0)} \rangle$, where $E_n^{(0)}$ is the nth energy level of $H^{(0)}$ and $|\psi_n^{(0)}\rangle$ is the corresponding eigenstate. As such, one adds to the Hamiltonian for the system of interest a correction term that is proportional to the operator of which one wants to calculate the expectation value. By plotting $E_n(\lambda)$ as a function of λ, one should obtain a straight line, the slope of which is $\langle W \rangle$. While this is potentially a very powerful procedure, there are two practical issues that can make it challenging to implement. First, any energy that is calculated by DMC will have an uncertainty that is typically at least 1% of the energy that is being calculated. As such, the range of λ that is being sampled must be sufficiently large to ensure that the variation in $E(\lambda)$ exceeds the size of the statistical fluctuations. In addition, λ must be kept small enough to ensure that the calculations are performed in the linear regime of $E(\lambda)$ vs λ. If the range of λ is too large, first order perturbation theory no longer applies and systematic errors will result. This means that some trial and error is necessary to determine the proper range of λ over which the calculations should be performed. In addition, each point in an E vs λ plot will require several DMC runs and at least four or five such points will be required to obtain a reliable slope.

In order to address the above issues, we have developed an adiabatic diffusion Monte Carlo (ADMC) scheme for evaluating expectation values that we find to be more efficient than the previously formulated approaches and which can be applied more systematically. As in the finite field approach, we base our evaluation of $\langle W \rangle$ on perturbation theory which says that for the Hamiltonian in Eq. (1), we can approximate $|\psi_n\rangle$ and E_n by

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \frac{\lambda^2}{2}|\psi_n^{(2)}\rangle + \cdots \tag{2}$$

and

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \frac{\lambda^2}{2} E_n^{(2)} + \cdots . \tag{3}$$

As before, the first order correction to the energy provides $\langle \psi_n^{(0)}|W|\psi_n^{(0)}\rangle$.

In a typical DMC simulation, E_0 is obtained by taking a time average of $E(\tau)$. In ADMC, our only modification is that we propagate $\hat{H}$ in Eq. (1) where λ is a linear function of τ. We choose $d\lambda/d\tau$ to be sufficiently small to ensure that over a single time step the change in the lowest eigenvalue of $\hat{H}(\lambda)$ is much smaller than the statistical fluctuations of the ADMC simulation. In this way, $\lambda\hat{W}$ in Eq. (1) is introduced adiabatically and the resulting $E(\tau)$ will fluctuate around the curve defined by Eq. (3) rather than a single energy level. If we choose the range of λ so that the calculated $E(\tau)$ can be fit to a low order polynomial in λ, the coefficient of the linear term in the expansion can be taken to be $\langle \psi_n^{(0)}|W|\psi_n^{(0)}\rangle$.

Another difficulty with using DMC techniques comes from the fact that energies and other properties of excited states cannot be obtained readily. One effective approach for calculating excited state energies involves the fixed node approximation, first proposed by Anderson.[10] In this approach, the wave function is forced to go to zero at specific configurations of the system. This is achieved by removing any walkers that cross a predefined nodal surface. While this approach is very powerful, it has a serious drawback in that it requires prior knowledge of the location of the nodal surface. Several authors have suggested that one can obtain an approximate nodal surface by defining its location in terms of a single parameter, η, that is a function of the internal coordinates of the system.[7,11] As long as the form of the approximate nodal surface is close to the position of the true node, this procedure will provide a good approximation to the energy of the excited state of interest.

In the fixed node approach the wave function is calculated on one side of the nodal surface, while the excited state energy, calculated by this method, should be independent of which part of the wave function is used. Therefore, one can determine the optimal location of the nodal surface by running a series of DMC simulations on either side of the node until the differences between these energies are smaller than the uncertainty of the approach. A major drawback of this approach is that locating the position of the node can be tedious.

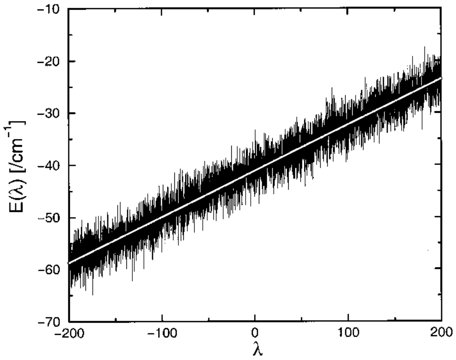

FIG. 1. Raw data used to calculate the B rotational constant for NeSH.

One way around this problem is to apply an adiabatic scheme similar to that proposed above for obtaining expectation values. In this approach, two DMC simulations are run, one for the part of the wave function that is on either side of the nodal surface. Once the two simulations are allowed to equilibrate for an initial position of the nodal surface, the position of the node, η, is varied linearly with time. At the end of the propagation, the energies obtained from the two simulations are plotted as functions of η on the same graph. The value of η where the two curves cross corresponds to the optimal position of the nodal surface and the energy gives the energy of that particular excited state. We find that when the range of η is relatively small, the $E(\eta)$ are approximated well by straight lines, permitting systematic determination of the location of the nodal surface.

III. RESULT AND DISCUSSION

The two approaches, described above, are tested by running ADMC simulations on NeSH and Ar_2HCl van der Waals complexes. For the NeSH system, the simulations are performed on the potential energy surface that was recently developed by some of us.[5] Following Cooper and Hutson,[6] the Ar_2HCl potential is approximated by a sum of the HFD-C of Ar_2 potential of Aziz and Chen[12] and the H6(3) ArHCl potential of Hutson.[13] The ADMC simulations are performed using 7000 walkers for NeSH and 10 000 walkers for Ar_2HCl, where all of the walkers are given equal weights. In these simulations, we employ a rigid body version of DMC that is based on the algorithm proposed by Buch.[4] The time steps of the ground state and excited state simulations are 100 and 20 a.u., respectively. The reported expectation values are the averages of the results of five simulations, with the exception of $\langle \cos\theta \rangle$ for NeSH where seven simulations are used. Five simulations are also used for each calculation of the excited state energies, when the node can be determined by symmetry and three simulations are used for the flexible node calculations. We have not employed the recrossing corrections in our calculations of the excited state energies, but, based on results of excited state

TABLE I. Comparison of expectation values from ADMC with the variational result for NeSH and Ar_2HCl.

System	Property	ADMC[a]	Exact[b]	% error
NeSH	$E_0{}^{\rm c}$ [/cm^{-1}]	$-41.11(0.08)$	-41.112	0.005
	$\langle R \rangle$ [/Å]	3.928(0.015)	3.907	0.5
	$\langle \cos\theta \rangle$	0.649(0.027)	0.6534	0.7
	B [/MHz]	2653(17)	2659.9	0.2
Ar_2HCl	$E_0{}^{\rm d}$ [/cm^{-1}]	$-323.17(0.07)$	-323.324	0.005
	A [/MHz]	1759.1(10.7)	1757.19	0.1
	B [/MHz]	1672.9(9.9)	1671.10	0.1
	C [/MHz]	851.4(8.9)	849.53	0.2

[a] Values in parentheses provide one standard deviation.
[b] Results reported in Ref. 5 for NeSH and Ref. 6 for Ar_2HCl.
[c] Calculated from 17 ADMC simulations.
[d] Calculated from 15 ADMC simulations.

simulations with $\Delta\tau=2$ to 50 a.u., we expect that this correction would raise the calculated excited state energies by approximately 1 cm^{-1}.

To illustrate how we use the ADMC approach to calculate expectation values, we have plotted, in Fig. 1, the raw results for the calculation of the B rotational constant for NeSH. In this simulation, $\lambda=-200$ at $\tau=0$. After the energy is stabilized, λ is increased by 0.05 for each of the next 8000 time steps. The choice of the range of λ is determined by two factors. First, we want to ensure that the change in E over the chosen range of λ is larger than statistical fluctuations. In addition, we want to keep the range of λ small enough that the energy is a linear function of λ. In the case of the results plotted in Fig. 1, the ADMC results fall in the linear regime. The accuracy of the linear fit can be checked by using a higher order polynomial in the fit. In this case the coefficients of higher order terms in the expansion are smaller than that of linear term at least by factor of 10^4.

In Table I, we present a variety of expectation values for NeSH and Ar_2HCl. Specifically we calculate expectation values of R, the Ne–SH distance; $\cos\theta$, where θ is the Ne–H–S angle; and $B=\hbar^2/2\mu R^2$. For Ar_2HCl, we calculate the A, B, and C rotational constants using the expressions given by Cooper and Hutson. Comparison with the results of variational calculations[5,6] shows that in all cases the error in the ADMC results is smaller than 0.75% while the uncertainty is approximately 1%. The largest error is found for the $\langle \cos\theta \rangle$. This is the only one of the reported quantities for which the range over which $E(\lambda)$ is linear is too small and a higher order expansion of E is needed to converge the expectation value.

An important aspect of these results comes in the relative ease with which they can be obtained. In contrast to the finite field scheme of Sandler *et al.*,[8(b)] where at least 25 simulations are required for each expectation value, each of the reported results is based on five simulations. In addition, by making λ a function of τ in the simulation, we have eliminated the possibly tedious search for the appropriate range of λ. We have also extended the acceptable range of λ by removing the constraint that $E(\lambda)$ be approximated by a linear fit. Finally, based on Eq. (3), the constant term in our fits of $E(\lambda)$ is E_0. Therefore, we can use the E_0 calculated from all of our runs on NeSH and Ar_2HCl to obtain the ground state energy for these systems. These results are also reported in Table I. For comparison, E_0 for NeSH and Ar_2HCl, obtained from five regular DMC simulations are $-41.05(0.07)$ and $-323.27(0.20)$ cm^{-1}, respectively.

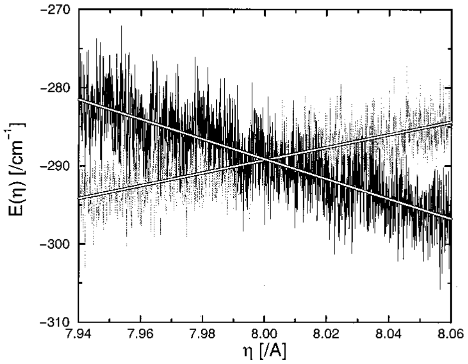

FIG. 2. Raw data used to calculate the energy of the fundamental in the breathing mode in Ar_2HCl.

Our evaluation of energies of excited states of van der Waals complexes follows a similar philosophy to that used for evaluating expectation values. When the position of the nodal surface can be defined by symmetry, for example for fundamental excitations in modes that are not totally symmetric, we use a fixed node approximation based on that node. For the totally symmetric modes we use ADMC to determine the location of the node and corresponding energy of these excited states. In Fig. 2, we plot raw results for a simulation of the fundamental in the breathing mode of Ar_2HCl, and the linear fits to these results. The gray and black data represent simulations of the wave function on either side of a node where $R_1+R_2=\eta$. Each simulation consists of 6000 time steps and η is increased by 2.1×10^{-5} Å at each time step. This data has been fit to the two white lines. The point at which the two lines cross provides the approximate location of the node and the corresponding energy. As with the calculation of the expectation values, because we are allowing η to vary linearly with time, we can use a crude simulation over a large range of η to locate the approximate location of the node. Once we have located the node, we can perform a second simulation over a much smaller region of η where $E(\eta)$ is expected to be approximately linear, and use linear fits of the raw data to calculate the position of the node and the corresponding energy.

TABLE II. Comparison of excited vibrational state energies of Ar_2HCl calculated using a fixed node ADMC approximation with those reported in Ref. 6. The locations of the nodes have been reported as footnotes.

Nodal surface[a]	DMC[b]	Ref. 6	% error
$\Theta=57.502°$	$-299.09(0.12)$	-298.35	0.2
$R_1=R_2$	$-297.78(0.34)$	-296.82	0.3
$\lvert R_1+R_2\rvert=8.000$ Å	$-289.02(0.20)$	-287.10	0.7
$\theta_1=\theta_2$	$-285.23(0.20)$	-283.74	0.5
Molecular plane	$-278.45(0.16)$	-276.64	0.7

[a] The internal coordinates used to describe the Ar_2HCl complex are the two Ar–HCl distances, R_j; the corresponding angles θ_j, where $\theta=0$ corresponds to the Ar–HCl geometry; and the Ar_1–HCl–Ar_2 angle, Θ.
[b] Calculated with $\tau=20$ a.u.; values in parentheses provide one standard deviation.

The resulting excited state energies for Ar_2HCl are reported in Table II. In general, the energies are within 1% of the values reported by Cooper and Hutson. Unlike the expectation values, where the statistical uncertainty is larger than the error, here the statistical uncertainty is much smaller than the error. The reason for this can be understood in terms of what is being calculated. We have approximated the lowest energy state with a node at a particular value of η. On the other hand, the nodal surface obtained in the exact calculations is much more complicated, and it is our simplifying approximation to the nodal surface that is leading to the $1-2\ \mathrm{cm}^{-1}$ errors in the predicted energies. In spite of this, the agreement between the ADMC results and those obtained from exact treatments is remarkably good.

IV. SUMMARY AND CONCLUSIONS

We have presented a systematic approach for using DMC to calculate ground and excited state properties of molecular clusters. The advantage of these methods comes from the fact that because a parameter is varied with τ through the simulation, we have simplified the search for the range of λ for calculations of expectation values and for the position of a nodal surface for fixed node calculations. Once the appropriate range of λ or η has been determined, the use of ADMC will minimize the number of simulations required to obtain the desired level of accuracy from the calculation. While DMC approaches are clearly not as accurate as approaches that are based on the variational principle, they scale favorably with system size, making studies of fairly large complexes tractable. It is our belief that the ADMC approaches outlined above will provide an important tool in future studies that employ DMC.

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