1 Diffusion Monte Carlo - general

Diffusion Monte Carlo was proposed by Anderson[2, 3] as a method for calculating ground state wavefunctions for molecular systems using statistical approaches. The method is based on the observation that the time-dependent Schrödinger equation (TDSE),

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2 \psi}{\partial x_i^2} + V(x)$$  \hspace{1cm} (1)

closely resembles the diffusion equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - kC. \hspace{1cm} (2)$$

One widely recognized way to solve the diffusion equation is through a random walk. For a given time step, $\Delta T$, the particles will move by a random amount where the random step sized $\Delta x$ satisfy

$$\overline{\Delta x} = 0 \hspace{1cm} (3)$$

and

$$\overline{\Delta x^2} = 2D \Delta t. \hspace{1cm} (4)$$

Often this is achieved by taking $\Delta x$ from a Gaussian random distribution[6] with the appropriate width. The second term on the right side of Eq. 2 provides the probability that a particular particle will be annihilated as a function of its coordinates.

If the time dependence of the TDSE $t$ is replaced by $\tau = i t / \hbar$, we obtain:

$$\frac{\partial \psi}{\partial \tau} = \frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{1}{m_i} \frac{\partial^2 \psi}{\partial x_i^2} - V(x), \hspace{1cm} (5)$$

it closely resembles the diffusion equation with the mass coefficient providing the diffusion constant and the potential, the probability that a particular diffusing particle (sometimes referred to as a walker or a psip) will be destroyed.

Since the TDSE equation in imaginary time has the long-time (large $\tau$) solution

$$\psi(x, \tau) = \psi_0(x) e^{-E_0 \tau} \hspace{1cm} (6)$$
leading to the result that DMC provides an approximate method for determining the ground state energy and wave function.

2 Computational Methods

Since we are solving the TDSE using random walk methods, we need to define the procedure for the particular problem. As was stated above, the step size for the random walk will be taken from a gaussian random distribution with FWHM = $\Delta \tau / m_i$ Once a step is made, the calculated energy is compared to

$$V_{\text{ref}} = V_{\text{avg}} - \frac{\alpha (N_e - N_0)}{N_0},$$

and

$$P_j = \exp \left[ - (V(x) - V_{\text{avg}}) \Delta \tau \right]$$

is evaluated for each of the psips. If $P_j > 1$ then the psip is in a classically allowed region and int($P_j$) - 1 replicas are generated at that configuration. The difference, $P_j - \text{int}P_j$ is compared to a random number taken from a uniform distribution on (0,1). If the random number is smaller than $P_j - \text{int}P_j$ an additional replica is generated at that configuration. If $P_j < 1$ then the configuration is classically forbidden and if a random number is smaller than the difference $1 - P_j$ then the replica is destroyed.

In Eq. (7), $\alpha$ is chosen so that the statistical fluctuations associated with the creation and destruction of psips is comparable to the statistical error of the Monte Carlo procedure.[4] For moderate sized $\Delta \tau$, $\alpha = 1 / \Delta \tau$, as suggested by Anderson,[2] provides a reasonable first guess. For smaller time steps, it may be necessary to modify the value of $\alpha$. On the systems tested, we find that a value of $\alpha$ that leads to the creation and destruction of $0.5 - 1\%$ of the psips seems to work quite well. Finally, $V_{\text{ref}}$ provides the zero-point energy of the system of interest and typical statistical fluctuations are approximately $1\%$ of the calculated energy. The corresponding wave function can be obtained by binning the distribution of psips either at one time or at several times.
3 Rotations

One difficulty of this approach for van der Waals systems comes from the fact that typically the intramolecular vibrational frequencies are two orders of magnitude larger than the intramolecular frequencies. This is particularly pronounced when there is one or more hydride stretching motions in the system. As a result, the zero-point energy of the van der Waals complex is the same order of magnitude as the fluctuations in the energies of the intramolecular vibrational zero-point energy. As a result, it would be preferable to run the dynamics either on an adiabatic potential where the intramolecular problem has already been solved or on for fixed intramolecular geometry. Several methods have been proposed for achieving this,[5, 1] and one that is particularly successful is the rigid body diffusion monte carlo approach proposed by Buch.

In contrast to the systems considered by Buch and by the approaches taken by her and others who have employed her approaches, we want to consider systems where linear geometries are energetically accessible. This leads to an important complication because once linear geometries are accessible the simple approach of Buch is no longer entirely valid. Before discussing the our approach, it is useful to consider the theory of finite rotations.

One way to describe the rotation of a diatomic molecule, defined by the vector $\vec{r}$ about its center of mass by an angle $\Theta$ with respect to the axis defined by $\vec{R}$, is given by:

$$\vec{r}' = R_\phi R_\theta \vec{r}$$  \hspace{1cm} (9)

where

$$R_\theta = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{pmatrix}$$ \hspace{1cm} (10)

$$R_\phi = \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$ \hspace{1cm} (11) \hspace{1cm} (12)

which gives
\[ \vec{r}' = \begin{pmatrix} \cos \phi & \cos \theta \sin \phi & \sin \theta \sin \phi \\ -\sin \phi & \cos \theta \cos \phi & \sin \theta \cos \phi \\ 0 & -\sin \theta & \cos \theta \end{pmatrix} \vec{r} \]  
(13)

\[ \approx \begin{pmatrix} 1 & \Omega_1 & 0 \\ -\Omega_1 & 1 & \Omega_2 \\ 0 & -\Omega_2 & 1 \end{pmatrix} \vec{r} \]  
(14)

The second expression provides the values of the matrix in the limit of small \( \theta \) and \( \phi \). Within this picture, one can either take \( \theta \) and \( \phi \) or \( \Omega_1 \) and \( \Omega_2 \) from a Gaussian random distributions with \( \vec{x}' = 3\Delta \tau / I \) where the factor of 3 comes from the fact that each displacement in an angle corresponds to displacements in 3-d space. For example, displacements with \( \vec{x}' = D \) in \( x, y \) and \( z \) is equivalent to taking displacements with \( \vec{r}' = 3D \) where \( r = \sqrt{x'^2 + y'^2 + z'^2} \).

The rest of the procedure works exactly as in the usual DMC propagations.

4 Results for M-SH

The above procedure has been checked for the M-SH \( A^2\Sigma^+ \) systems with \( M = \text{Ne} \) and \( \text{Kr} \). We used time steps of 100 a.u. and ran for propagation times of approximately 80 000 a.u. For Kr-SH, the zero-point energy is -1291 cm\(^{-1}\). Statistical measures of the energy gave results of approximately \(-1286 \pm 10 \text{ cm}^{-1}\) when the propagation was run in three-dimensions (the \( z \) axis was defined to be the Kr-SH vector). For Ne-SH, we calculate a zero-point energy of \( 42.5 \pm 2.2 \text{ cm}^{-1} \) from both three-dimensional and full, eight-dimensional calculations. The variational energy for this system is -43.7 cm\(^{-1}\).

5 Code

See attached appendix.
References


