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Diffusion Monte Carlo simulations of the dipole-bound state of the water dimer anion

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It is shown how the diffusion quantum Monte Carlo method for solving the Schrödinger equation can be adapted to calculate the lowest energy state of a dipole-bound cluster anion. Specifically, the method can be used to calculate the rotationally adiabatic potential curve that arises due to the interaction of an electron with a dipolar molecular cluster. The theory allows the motion of each monomer molecule to be coupled explicitly with the angular motion of the electron. Application is made to the anion of the water dimer. The method gives a clear picture of the reorientation of the monomer water molecules that produces an overall dipole moment for the water dimer that is favorable for forming a dipole-bound state with the electron. © 1999 American Institute of Physics. [S0021-9606(99)00745-X]

I. INTRODUCTION

Theoretical studies have suggested that an electron in a dipolar field can form a bound state if the dipole moment of the molecule is greater than ~ 2.5 Debye.¹ There have been many experiments^{2–5} that have confirmed this prediction and now over 30 such dipole-bound anions have been observed for molecules ranging from formaldehyde to uracil.⁶ A particular feature of these dipole-bound anions is that their geometries are almost identical to those of the neutral parent molecules, indicating the absence of valence forces binding the electron.

These experimental results can be explained by remarkably simple theories.¹ For example, just diagonalizing a simple electron–dipole interaction potential with a basis set that couples angular momenta of the electron and molecular rotation gives an effective potential on which the electron moves. Solving for the motion of the electron on this one-dimensional radial potential gives bound states, scattering resonances and widths for the dipole-bound electron.⁷ This simple “rotationally adiabatic” theory explained and predicted subtle features of the photodetachment spectra for electrons bound to polar radicals,³ including isotope effects,⁸ for anions such as CH_2CN^- and CH_2CHO^- . The model was later extended by Schermann and co-workers to explain the variation in electron affinity of a large number of dipole-bound states of anions.⁶

Ab initio calculations have also been applied extensively to these special anions.^{9–14} In particular, there have been several recent such applications to electrons attached to water clusters.^{13–15} However, dipole-bound states are hard to treat by conventional *ab initio* theory due to the very diffuse nature of the orbital of the weakly-bound electron and the very small electron affinities (typically less than 50 meV). Furthermore, as the electron affinities in these systems have similar magnitudes to rotational energies, there will be strong coupling between the orbital motion of the electron and the rotational motion of the parent molecule. It is necessary to

apply a theory beyond the Born–Oppenheimer approximation to describe this coupling properly.

Negatively charged molecular clusters have been the subject of several experiments and calculations and they also can form dipole-bound states.^{9,16,17} Even if a monomer molecule in a cluster has a dipole moment less than 2.5 Debye, the different molecules in the cluster can align to produce an overall dipole moment for the cluster larger than 2.5 Debye so that a dipole-bound state can be formed.¹⁵ However, such alignment of dipoles competes with the weak intermolecular forces in the neutral cluster and so studies of such dipole-bound cluster anions might give information on the intermolecular forces and structure of the parent neutral cluster.

A classic example of this is the water dimer anion $(\text{H}_2\text{O})_2^-$, the smallest stable negatively charged cluster of water molecules. An individual water molecule has a dipole moment of 1.85 Debye and does not form a dipole-bound state, whereas $(\text{H}_2\text{O})_2^-$ does. This was predicted by several theoretical studies including *ab initio* calculations and path integral simulations.^{18–20} The earlier theoretical studies predicted a geometry for the ion very similar to that for the neutral.^{18–20} However, more recent electronic structure calculations have suggested that one of the water monomers rotates so that the dipole moments of both monomers can align.¹⁵ This enables the water dimer to have a larger overall dipole moment that can more easily bind the electron.

Experiments on $(\text{H}_2\text{O})_2^-$ were first done by Haberland *et al.* who observed the detachment of the electron in an external field.²¹ They estimated an electron affinity of 17 meV. More recently, Coe *et al.* measured the vertical detachment energies to be 40 meV.²² They also observed weak vibrational features suggesting that the negative dimer ion has a slightly different geometry to the parent neutral dimer. Similar conclusions were also made by Bouteiller *et al.* who used a Rydberg electron transfer experiment to give an adiabatic electron affinity of 30 ± 4 meV.¹⁵ They also reinterpreted the experimental results of Haberland *et al.* to give an adiabatic electron affinity of 30 meV. A review of different

measurements of the adiabatic electron affinity for $(\text{H}_2\text{O})_2^-$ gives experimental values ranging from 12 meV to 30 meV.⁶

The theoretical studies have given much insight into $(\text{H}_2\text{O})_2^-$ but a theory is still required that is capable of giving a detailed treatment of the coupling between the orbital angular momentum of the electron and the rotational motion of the monomer molecules in dipole-bound cluster anions such as $(\text{H}_2\text{O})_2^-$. Such a theory is presented in this paper. We modify the rotationally adiabatic theory that one of us previously developed to explain the photodetachment spectra of electrons bound to polar radicals⁷ and describe how the method can be applied to dipole-bound cluster anions. In particular, we show how this theory can allow the individual monomers in a cluster to rotate so that a favorable balance is achieved between the intermolecular forces and attractive electron–dipole interactions. We apply the theory to $(\text{H}_2\text{O})_2^-$.

To apply the rotationally adiabatic theory⁷ to a weakly bound cluster, it is first necessary to solve the Schrödinger equation for the rotational motion of each monomer in the cluster coupled to the angular motion of the electron, which has a fixed distance from the center of mass of the parent cluster. Even for $(\text{H}_2\text{O})_2^-$, this is an eight-dimensional problem which is very hard to solve using conventional methods. An alternative method for solving a Schrödinger equation to obtain a ground state energy is diffusion quantum Monte Carlo (DQMC).²³ This method has been particularly successful in its applications to weakly bound water clusters.^{24–28} Here we show that DQMC is an ideal algorithm for solving the multidimensional Schrödinger equation arising in the rotationally adiabatic theory for dipole-bound anions of molecular clusters. This is demonstrated through application to $(\text{H}_2\text{O})_2^-$.

In Sec. II we introduce the rotationally adiabatic theory for electron–dipole bound states and describe how the DQMC method is incorporated in the theory for cluster anions. In Sec. III we describe numerical details of the method. Test calculations are reported in Sec. IV on H_2O^- for which DQMC results are compared with those obtained with a basis set method. In Sec. V, we report results obtained applying the DQMC method to $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$. We show that the method is capable of giving a detailed picture of the competition between directional hydrogen bonding and attractive electron–dipole interaction, the balance of which determines the structure of $(\text{H}_2\text{O})_2^-$. In Sec. VI we conclude that the rotationally adiabatic DQMC approach will be a useful theory in applications to the dipole-bound states of cluster anions.

II. THEORY

A. Potential function

The potential energy model for electron–dipole complexes first used to calculate photodetachment spectra,⁷ and extended by Schermann and co-workers to calculate the electron affinities of many dipole-bound states,⁶ is extended here to the interaction of an electron with a weakly bound cluster of N monomer molecules. Since the electron is extremely

weakly bound with a very diffuse orbital, it is appropriate to approximate it as an individual particle with no exchange interaction with the other electrons.¹

First, the leading terms in the multipole expansion for the interaction of the electron with each monomer molecule are evaluated and summed

$$V_e = \sum_{j=1}^N \left(-\frac{\alpha_j}{2R_j^4} - \frac{\mu_j \cos \theta_j}{R_j^2} \right) f(R_j) + V_s(R), \quad (1)$$

where R_j is the distance from the electron to the center of mass of monomer j which has polarizability α_j and dipole moment μ_j . In addition, R is the distance from the electron to the center of mass of the whole cluster. Also, the orientation of the monomer dipole with respect to the vector \mathbf{R}_j joining the electron to the center of mass of monomer j is θ_j . In addition we include the damping function⁷

$$f(R_j) = [1 - \exp\{-(R_j/R_0)^6\}]. \quad (2)$$

In calculations and comparisons with experiment on several dipole-bound anions, Schermann *et al.* found that an appropriate form for the short range repulsive interaction of the dipole-bound electron with the other electrons of the parent molecule is

$$V_s(R) = \exp[-(R/R_c)^6] \quad (3)$$

with $R_c = (\alpha)^{1/3}$, where α is the polarizability of the molecule.⁶

B. Rotationally adiabatic potentials

The previous applications of the rotationally adiabatic theory to electron–dipole metastable and bound states^{6,7} involved a diagonalization of the potential V_e with an angular basis set on a grid of fixed values of the distance R of the electron to the center of mass of the molecule. The angular basis set was defined in space-fixed coordinates in which the rotational motion of the parent molecule was coupled with the orbital motion of the electron. The diagonalization for total angular momentum $J=0$ gives one rotationally adiabatic potential curve $\epsilon(R)$ that remains attractive for smaller R ; all other excited state curves are strongly repulsive for small R for monomer dipole moments less than 9.8 Debye.²⁹ This simplification enables the bound state and scattering dynamics of the electron to be determined by the single rotationally adiabatic potential curve $\epsilon(R)$.⁷ An important aspect of this theory is that the rotational motion of the molecule and the orbital motion of the electron are coupled together explicitly and so the normal Born–Oppenheimer approximation that separates these coordinates is not imposed. The monomer neutral molecule is treated as rigid, although it is straightforward to relax this restriction by including the intramolecular vibrational modes if the dipole moment of the molecule depends particularly strongly on these.

For a dipole-bound cluster anion with vector \mathbf{R} defined from the electron to the center of mass of the cluster (Fig. 1), the Hamiltonian that needs to be diagonalized for total angular momentum $J=0$ and fixed distance $R=|\mathbf{R}|$ is

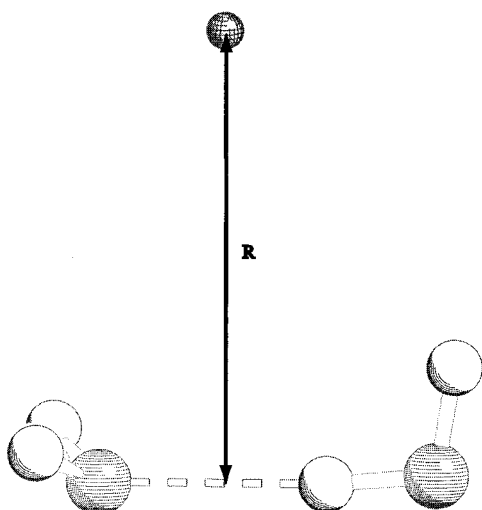


FIG. 1. Coordinates for $(\text{H}_2\text{O})_2^-$. R is the distance of the electron from the center of mass of $(\text{H}_2\text{O})_2$.

$$H_a = \sum_{j=1}^N \hat{K}_j^2 + \sum_{j=1}^N \hat{T}_j^2 + \frac{\hat{L}^2}{2R^2} + V_c + V_e. \quad (4)$$

Here, \hat{K}_j^2 and \hat{T}_j^2 are the operators that represent, respectively, the rotation of the principal axes and translational motion of monomer j with respect to a set of space-fixed axes. Also, \hat{L}^2 is the electron orbital angular momentum operator that describes the orientation of \mathbf{R} .⁷ In addition, V_c is the potential energy surface for the parent neutral cluster.

Diagonalization of H_a gives $\epsilon(R)$ and the wave function $\Psi_a(Q;R)$, where the compound variable Q represents collectively the angles of rotation and translational motion of all the monomer molecules and the angular motion of the electron. Finally the Hamiltonian for the radial motion of the electron

$$H_r = -\frac{1}{2} \frac{d^2}{dR^2} + \epsilon(R) \quad (5)$$

is diagonalized to give the electron energy E and radial wave function $\Psi_r(R)$. The final wave function for the cluster anion is then

$$\Psi = \Psi_a(Q;R) \Psi_r(R) \quad (6)$$

from which properties such as the overall dipole moment and rotational constants of the cluster can be evaluated.

C. Diffusion Monte Carlo

The DQMC method gives the lowest energy level of a multidimensional Hamiltonian such as Eq. (4) so that $\epsilon(R)$ can be constructed for a cluster anion. In DQMC, an analogy is drawn between the diffusion equation and the time-dependent Schrödinger equation.²³ Since the diffusion equation can be solved with a random walk algorithm, then the same is true for the time-dependent Schrödinger equation. It is straightforward to show²³ that for long times, this method

projects out the ground state energy of the Schrödinger equation and that is exactly what is needed in the rotationally adiabatic theory.

The DQMC method is described in detail elsewhere^{23,24} and only a brief summary will be given here. Consider a single particle with mass m , having coordinate x and moving in a potential $V(x)$. The time-dependent Schrödinger equation is

$$-i\hbar \frac{\partial \psi(x,t)}{\partial t} = \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,t)}{\partial x^2} - V(x) \psi(x,t). \quad (7)$$

Substituting for imaginary time

$$\tau = it/\hbar \quad (8)$$

gives

$$\frac{\partial \psi(x,\tau)}{\partial \tau} = \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x,\tau)}{\partial x^2} - V(x) \psi(x,\tau) \quad (9)$$

which is of the form of a diffusion equation plus a first-order rate term

$$\frac{\partial C}{\partial \tau} = D \frac{\partial^2 C}{\partial x^2} - kC \quad (10)$$

with

$$D = \frac{\hbar^2}{2m}.$$

Equation (10) has the solution

$$\psi = \sum_{i=0} c_i g_i(x) \exp(-[E_i - E_{\text{ref}}]\tau), \quad (11)$$

where $\{g_i(x)\}$ are the set of bound states with energies $\{E_i\}$ and E_{ref} is the zero of energy. If $E_0 = E_{\text{ref}}$ then the only state that does not decay to zero in Eq. (11) as τ gets large is the ground state $g_0(x)$.

Thus DQMC projects out the ground state eigenfunction and eigenvalue providing equation (10) can be propagated for large τ . For a small displacement of the imaginary time-step $\Delta\tau$, with position $x(0)$ at $\tau=0$, the solution to Eq. (9) can be written as

$$\begin{aligned} \psi(x, \Delta\tau) = & \psi(x, 0) (4\pi D \Delta\tau)^{-3/2} \exp\{-[x - x(0)]^2 / 4D \Delta\tau\} \\ & \times \exp[-(V(x) - E_{\text{ref}})\Delta\tau]. \end{aligned} \quad (12)$$

The x -dependent Gaussian part of this solution is modelled with a Monte Carlo distribution of x values with the restriction that the standard deviation of the distribution is set to the mean value of the Gaussian function. These values are called "replicas." The exponential function that depends on $V(x)$ and $\Delta\tau$ provides a weight for each replica. After this process is repeated for many steps in τ , the histogram of weights represents the wave function. A significant advantage of the above procedure is that the same method can be applied to deal with the x , y , and z coordinates of any number of particles. Therefore, it is straightforward to perform the DQMC calculations for multidimensional systems.

It is advantageous also to exploit a rigid-body DQMC algorithm (RB-DQMC).³⁰ In this approach, the high-frequency vibrations of the monomer molecules are com-

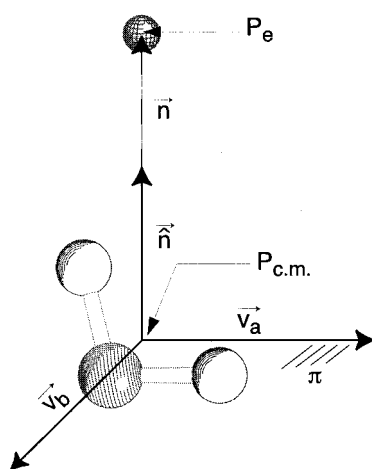


FIG. 2. Coordinates that describe the rotation of the electron in a cluster anion.

pletely factorized out from the problem. Consequently, the only modification to the conventional DQMC algorithm for a neutral cluster is that the random displacements of coordinates are done for the rotational angles and center of mass of each monomer, not for the Cartesian coordinates of each atom in the monomer. This enables the calculations to be performed with much longer time steps than in conventional DQMC.²⁸ In application to dipole-bound cluster anions, this is an important advantage of the algorithm as the RB-DQMC calculations have to be repeated several times to produce $\epsilon(R)$.

D. Rotation of the electron

A feature not met in RB-DQMC computations on neutral clusters is the treatment of the rotational motion of the electron for fixed R distances. Knowing the cartesian coordinates of the electron $P_e = (x_e, y_e, z_e)$ and center of mass of the cluster $P_{c.m.} = (x_{c.m.}, y_{c.m.}, z_{c.m.})$ it is easy to construct a vector $\vec{n} = {}^t P_e - {}^t P_{c.m.}$ that determines one of the principal axes of rotation of the electron. The normalized vector along \vec{n} has the components $\{\hat{n}_x, \hat{n}_y, \hat{n}_z\}$. The remaining two principal axes can be described as two real vectors \vec{v}_a and \vec{v}_b , which are both perpendicular to \vec{n} and to each other, therefore forming an orthogonal basis. Note that these two vectors belong to the plane π perpendicular to the vector \vec{n} passing by $P_{c.m.}$ (see Fig. 2). We can define \vec{v}_a and \vec{v}_b analytically by

$$\vec{v}_a = \begin{pmatrix} -\sqrt{\hat{n}_y^2 + \hat{n}_z^2} \\ \hat{n}_x \hat{n}_y \\ \sqrt{\hat{n}_y^2 + \hat{n}_z^2} \\ \hat{n}_x \hat{n}_z \\ \sqrt{\hat{n}_y^2 + \hat{n}_z^2} \end{pmatrix}, \quad \vec{v}_b = \begin{pmatrix} 0 \\ \hat{n}_z \\ -\sqrt{\hat{n}_y^2 + \hat{n}_z^2} \\ \hat{n}_y \\ \sqrt{\hat{n}_y^2 + \hat{n}_z^2} \end{pmatrix}. \quad (13)$$

Using the two axes from Eq. (13), we can define two rotations about them $\mathbf{R}_a = [\theta_a, \vec{v}_a]$ and $\mathbf{R}_b = [\theta_b, \vec{v}_b]$. In the RB-DQMC algorithm, the values of the two angles are each given by a Gaussian distributed random number with mean $\mu=0$ and standard deviation $\sigma = \sqrt{\Delta\tau/R^2}$.

We apply the rotation to the electron coordinates in the following order:

$$\vec{n}' = \mathbf{R}_{tot} \vec{n} = \mathbf{R}_a (\mathbf{R}_b \vec{n}). \quad (14)$$

A quaternion algorithm in its vector operator formulation is used to perform the rotations to keep numerical errors to a minimum.³¹

E. Algorithm

The algorithm we use for calculating the rotationally adiabatic potential curve $\epsilon(R)$ for an electron interacting with a cluster of N rigid molecules using RB-DQMC is as follows.

(1) A set of fixed distances $\{R\}$ of the electron from the center of mass of the cluster is chosen.

(2) For one of these R distances, we apply a RB-DQMC procedure to the N rigid molecules; namely, we perform a random translation of the center of mass of each molecule and a random rotation of each rigid body about its three inertia axes. We use the rotation described in equation (14) to carry out the necessary random angular displacement of the electron about the center of mass of the dipolar system. After removing the total translation of the center of mass of the system, the total potential energy ($V_c + V_e$) is evaluated and used in the remaining standard DQMC algorithm.²³ This procedure is equivalent to obtaining the eigenvalue of lowest energy of the Hamiltonian of Eq. (4) and gives the required energy $\epsilon(R)$ and wave function $\Psi_a(Q;R)$ at the chosen R value. Properties of the wave function [such as the dipole moment $\mu(R)$] are calculated at each value of R by using the descendant weighting procedure.²³

(3) Repeating calculation (2) for different R values gives an effective potential curve $\epsilon(R)$ that can be fitted to a suitable function that includes terms in R^{-2} and R^{-4} .

(4) Diagonalization of the radial Hamiltonian of Eq. (5) using a basis set of equally spaced distributed Gaussian functions gives the radial wave function $\Psi_r(R)$ and energy E of the single electron-dipole bound state of the cluster anion. The electron affinity is then $-E$. Final properties can then be calculated by using $\Psi_r(R)$ to average the properties calculated in step (2) over R .

The above approach is general and, in principle, can be applied to a cluster anion of any size if a suitable potential surface V_c for the parent neutral cluster is available. If the interaction of an electron with the cluster is treated as a sum of interactions with each monomer, then the potentials V_e can easily be constructed, but it is straightforward also to include more elaborate many-body terms such as induction terms in the electron-cluster interaction potential in an analogous way that can be done for neutral clusters.³² However, a crucial need of the theory is the full rigid-body potential V_c of the neutral cluster. Thus, this rotationally adiabatic-DQMC theory is an ideal and natural way of extending the useful information on the potentials and structures of neutral clusters to cluster anions with dipole-bound states. In the next section we apply the method to $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$.

Application of DQMC to calculate adiabatic or effective potential energy curves has been done before in various contexts such as the calculation³³ of the low-lying vibrational

states of $(\text{HF})_2$ and in computing the zero-point energy along a path of a chemical reaction.³⁴ We are unaware, however, of a previous application of the method to dipole-bound cluster anions.

III. CALCULATION DETAILS

In the application of the theory described in Sec. II to $(\text{H}_2\text{O})_2^-$, a polarizability of 1.45 \AA^3 and dipole moment of 1.853 D were used for each water monomer.³⁵ For $(\text{D}_2\text{O})_2^-$ the same monomer dipole was used with a polarizability of 1.26 \AA^3 . In addition, the short-range parameter in the pseudopotential of Eq. (2) was set to $R_0=4$ bohr as Schermann *et al.* found that the optimum values for R_0 were all close to this value when the rotationally adiabatic theory was used to fit experimental electron affinities of 17 different dipole-bound anions.⁶

The DQMC computations were done with 1000 replicas and pre-equilibration loops of 100 steps of 60 a.u. each until the standard error of the energy was smaller than 0.5%. After equilibration, 100 steps of 30 a.u. each were taken until the standard error of each energy was smaller than 0.1%. In the separate DQMC computations, the electron was held at fixed distances of 50, 40, 30, 20, 15, 12, 10, 9, and 8 Å from the center of mass of the dimer.

The adiabatic potential curves were fitted to a function of the form

$$\epsilon(R) = -\frac{C}{R^2} - \frac{D}{R^4}. \quad (15)$$

For $(\text{H}_2\text{O})_2^-$, the parameters obtained were $C=19\,395 \pm 226 \text{ cm}^{-1} \text{ \AA}^2$ and $D=461\,428 \pm 18\,000 \text{ cm}^{-1} \text{ \AA}^4$. For $(\text{D}_2\text{O})_2^-$, the parameters were $C=18\,988 \pm 253 \text{ cm}^{-1} \text{ \AA}^2$ and $D=467\,527 \pm 20\,100 \text{ cm}^{-1} \text{ \AA}^4$. The overall dipole moment of $(\text{H}_2\text{O})_2^-$ was fitted to the form

$$\mu(R) = a + \frac{b}{R^c + d} \quad (16)$$

and the constants $a=2.749$, $b=73$, $c=2.28$, $d=89$ (with R in units of Å, and the dipole in Debye) were obtained.

Equation (5) was diagonalized with 98 Gaussian functions equally distributed between $R=1.0$ and 98.0 bohr, with an overlap between adjacent Gaussian functions of 0.690. The V_c potential for $(\text{H}_2\text{O})_2$ used in the simulations was due to Watts and co-workers (the RWK2 potential).³⁶ This is a simple and realistic potential for $(\text{H}_2\text{O})_2$. It is not as sophisticated as some recently proposed potentials,³² but is computationally cheap to evaluate and is a reasonable potential to use in the first application of our method. A dipole moment of 2.76 D is obtained for $(\text{H}_2\text{O})_2$ in the DQMC simulations with this potential.

IV. CALCULATIONS ON WATER ANION

As a rigorous test of the RB-DQMC theory for cluster anions described in Sec. II, we calculated the rotationally adiabatic potential curve $\epsilon(R)$ for H_2O^- . This is a problem simple enough to be treated also with the basis set method.⁷ The parameters given in Sec. III were used in these calculations. Figure 3 shows a comparison of the $\epsilon(R)$ for H_2O^-

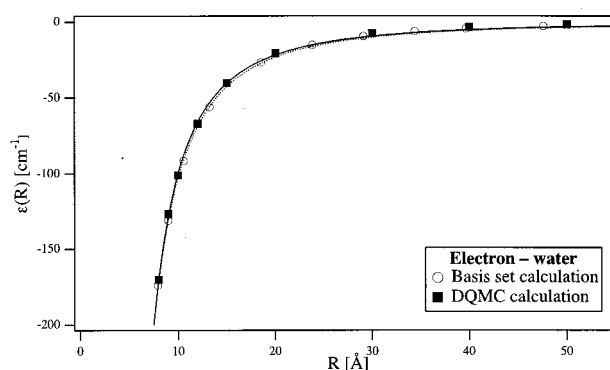


FIG. 3. Rotationally adiabatic potential curves $\epsilon(R)$ for H_2O^- , obtained with the present DQMC method and a basis set method (Ref. 7).

calculated with the RB-DQMC and basis set methods. The agreement is excellent. This is a firm test of the procedures described in Sec. II and shows that the RB-DQMC method obtains the lowest eigenvalue of Eq. (4) accurately.

V. RESULTS FOR WATER DIMER ANION

In Fig. 4 we show the rotationally adiabatic energy curves $\epsilon(R)$ for $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$. These have been calculated with the DQMC theory and parameters described in Secs. II and III. It can be seen that $\epsilon(R)$ starts to get strongly attractive for values of R below 15 Å. The $\epsilon(R)$ curve for $(\text{D}_2\text{O})_2^-$ is indistinguishable on the scale of the diagram from that for $(\text{H}_2\text{O})_2^-$.

Figure 5 gives the calculated overall dipole moment $\mu(R)$ of $(\text{H}_2\text{O})_2^-$ as a function of R . Also shown in this figure are the vibrationally averaged structures of $(\text{H}_2\text{O})_2^-$ obtained from the DQMC simulations for different R values. For very large R , the dipole moments of the two monomer water molecules in the ground vibrational state do not align to give the largest possible overall dipole moment of the molecule, with the intermolecular forces in the neutral cluster determining the geometry of $(\text{H}_2\text{O})_2$ as shown. However, the calculated $\mu(R)$ increases significantly as R decreases, and the cluster structures show that one water molecule flips to a more favourable geometry so as to give a larger overall dipole of $(\text{H}_2\text{O})_2$ at smaller values of R . This gives stronger

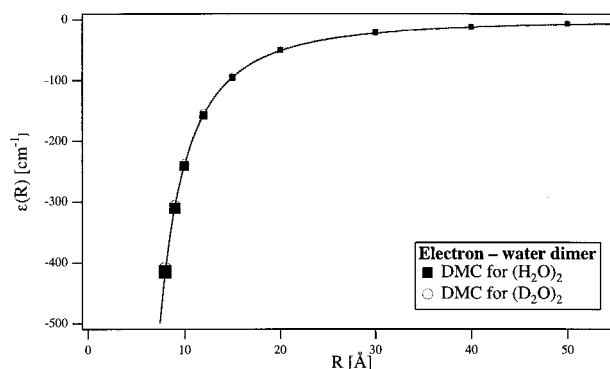


FIG. 4. Rotationally adiabatic potentials $\epsilon(R)$ for the dipole-bound electron in $(\text{H}_2\text{O})_2^-$ (squares) and $(\text{D}_2\text{O})_2^-$ (circles). The statistical error in the energy points is indicated by the size of the symbols.

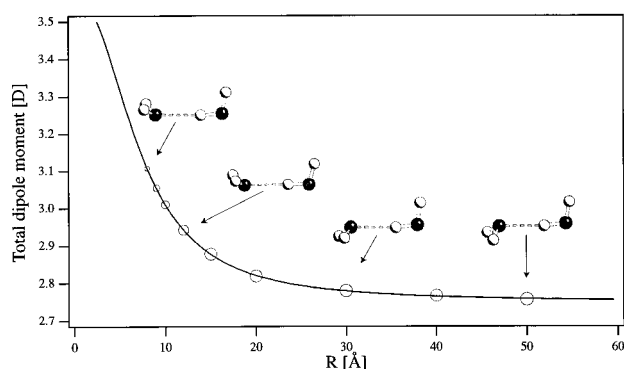


FIG. 5. Total dipole moment $\mu(R)$ for $(\text{H}_2\text{O})_2^-$ plotted against R . Also shown are the geometries of $(\text{H}_2\text{O})_2^-$ obtained from the DQMC calculations for selected R values. Note the change of structure for small R to produce a larger $\mu(R)$.

bonding with the electron but a slightly weaker contribution from the potential energy surface of the neutral dimer. The final calculated dipole moment for $(\text{H}_2\text{O})_2^-$, averaged over R , was 3.09 D. Note that this dipole moment is larger than the value of 2.5 D needed to form a dipole-bound state¹ and is also larger than the value of 2.76 D for neutral water dimer when $R \rightarrow \infty$.

The simulations show that the DQMC method provides a very clear picture of the competition between alignment of the two monomer dipoles to maximize the attractive electron-dipole interaction and the directional intermolecular forces that control the hydrogen bonding in the neutral cluster. Such a competition would become even more severe for water clusters larger than the dimer since the lowest energy isomers of neutral $(\text{H}_2\text{O})_n$ clusters have cyclic structures²⁷ and this is not the most favorable alignment for the largest overall dipole of the cluster, which would be favored by a chain of water monomers.

Figure 6 shows the probability distribution

$$P(R) = [\Psi_r(R)]^2$$

for the radial electron density superimposed on $\epsilon(R)$ for $(\text{H}_2\text{O})_2^-$. There is a large contribution to $P(R)$ for R values less than 10 Å and the distribution extends out to 30 Å. The calculated adiabatic electron affinity is 24.1 meV for $(\text{H}_2\text{O})_2^-$ and 27.0 meV for $(\text{D}_2\text{O})_2^-$. We do not consider the differ-

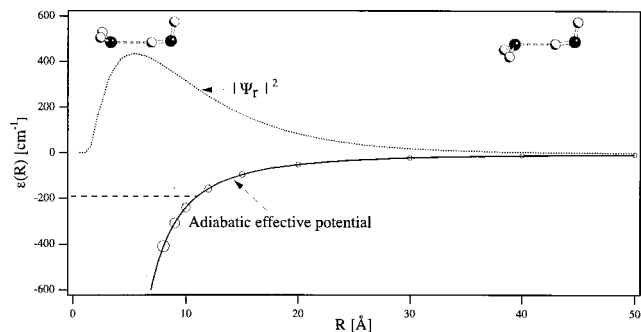


FIG. 6. Plot of $[\Psi_r(R)]^2$ against R for the dipole-bound electron in $(\text{H}_2\text{O})_2^-$. The dashed line shows the ground state energy of $E = -194.3 \text{ cm}^{-1}$.

ences between the results for $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$ to be significant, given the uncertainties in the parameters of Eq. (15) which essentially bring $\epsilon(R)$ for both ions to the same values within the statistical error. Considering the approximations made in the theory, these results compare quite well with the latest experimental values¹⁵ of $30 \pm 4 \text{ meV}$ for $(\text{H}_2\text{O})_2^-$ and $26 \pm 4 \text{ meV}$ for $(\text{D}_2\text{O})_2^-$. We note also that a review of all the different measurements of the electron affinity for $(\text{H}_2\text{O})_2^-$ gives experimental values ranging from 12 meV to 30 meV.⁶ Our results suggest that there should be essentially no difference between the electron affinities for $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$, and the experimental values for the two ions are the same within their error estimates.¹⁵

VI. CONCLUSIONS

A rotationally adiabatic theory for dipole-bound states is developed to treat molecular cluster anions. The theory explicitly treats the coupling between rotational and translational motion of the monomer molecules and the orbital motion of the electron. This is achieved by application of a rigid body diffusion quantum Monte Carlo algorithm for computing the ground vibrational state of a multidimensional Schrödinger equation.

The theory is tested on H_2O^- by comparing with a rotationally adiabatic potential curve calculated with a basis set method. The theory is then applied to $(\text{H}_2\text{O})_2^-$ and $(\text{D}_2\text{O})_2^-$. The geometry of $(\text{H}_2\text{O})_2^-$ is determined by the water monomer molecules taking up positions that balance the need to produce a strong hydrogen bond and the most attractive electron-dipole interaction. This balance of intermolecular and electron-dipole forces is shown very clearly in the DQMC simulations. It is found that the averaged structure of $(\text{H}_2\text{O})_2^-$ is different to that of $(\text{H}_2\text{O})_2$ with a flipping of the H atoms of one monomer to yield a stronger overall electron-dipole interaction. This is also the conclusion of recent density functional calculations.¹⁵ The theory is a general one and should be applicable to dipole-bound states of larger cluster anions and monomers other than H_2O , providing an appropriate intermolecular potential surface is available for the neutral cluster.

Several extensions of the theory presented here should be possible. The description of the attractive interaction between the electron and the monomer can be improved by using more terms in the expansion and many-body terms. The short-range semiempirical pseudo-potential used in the present calculations to describe the repulsive interaction of the dipole-bound electron with the other electrons in the cluster might be improved in various ways. One approach that would make this repulsive term purely *ab initio* would be to use intermolecular perturbation theory.³² Another ambitious calculation that is suggested by the present new application of the DQMC theory, and is also suggested by a previous computation linking vibrational DQMC with an *ab initio* electronic structure code,³⁷ is to treat the coordinates of all the electrons and the nuclei of the cluster anion simultaneously in a full DQMC calculation. This approach would

give an exact ground state wavefunction for the dipole-bound cluster anion and would give definitive results for the problem.

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