Electron localization in water clusters. I. Electron–water pseudopotential

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A local pseudopotential for the interaction of an electron with a water molecule in the electronic ground state is developed. The potential contains Coulomb, adiabatic polarization, exclusion, and exchange contributions. The potential is suitable for a description of excess electron states in water clusers, and for studies of electron solvation in water. Quantum path integral molecular dynamics simulations of electron localization in water clusters employing this potential yield results in agreement with available experimental data and all-electron quantum chemical calculations.

I. INTRODUCTION

The nature of excess electrons in fluids has been the subject of numerous experimental and theoretical investigations since the discoveries of solvated electron states in bulk liquid ammonia[1] and in water.[2] The range of systems in which electron localization has been explored covers a wide spectrum of chemical species, types of interactions, and ambient conditions.[3–9] These systems include dense and sub- and supercritical polar vapors (NH_3, H_2O),[10,11] liquid water and ammonia,[1–9] rare gases,[12–18] nonpolar[19] and hard-sphere fluids,[20–22] and molten alkali halides.[23–25] In addition, in more recent studies, the attachment of an electron to small molecular clusters of polar molecules [$(H_2O)_n$ and $(NH_3)_n$][26–31] and alkali halide clusters[32,33] has been investigated.

Theoretical studies of excess electron localization in polar liquids constitute some of the early explorations of electronic states of liquids. Cavity models for electron localization in polar solvents were proposed 40 years ago.[34,35] A significant development involved the application of Landau's large polaron theory[36] to the polar liquid.[37–40] Early theoretical studies,[39,40] of electron solvation in bulk polar fluids employed dielectric continuum models where the reaction of the medium to the excess electron is modeled via polarization of the medium, which results in self-trapping of the electron in a "cavity." Subsequent work recognized the discrete nature of the first solvation layer, accounting roughly for the repulsive and attractive short-range electron solvent interactions, while employing the continuum approximation for long-range attractive interactions.[41–45] These "semicontinuum models" advanced energetic stability conditions for electron localization in fluids, providing approximate descriptions of configurational diagrams of the excess electron center in its ground and excited electronic states.[41–46] These studies rested on grossly oversimplified potentials (or model potentials) for the electron–solvent interaction in the first coordination layer[41–46] and beyond it.[47,48] A more refined approach to the problem of electron solvation in bulk water consisted of unrestricted Hartree–Fock calculations for a discrete cluster of four water molecules in a prescribed orientation, containing an excess electron, embedded in a dielectric continuum.[49] In addition, the attachment of electrons to water and ammonia clusters has been investigated using quantum-chemical calculations.[50,51] The semicontinuum approaches,[42–46] which rest on a rather primitive description of electron–solvent interactions in the first coordination layer, and which neglect the discrete molecular structure, do not provide an adequate description of the molecular reorganization processes accompanying the electron localization and of the local potential felt by the electron. The quantum-chemical approaches[49–51] are limited to small static clusters, and due to computational constraints do not afford an exhaustive search in the multidimensional configuration space for the minimum energy structure.

The recent application of the Feynman path-integral formulation of quantum statistical mechanics[52–57] to systems involving the interaction of an electron with a many-body classical system alleviates the problems which hamper the above treatments. The application of this method, however, requires tractable interaction potentials between the classical components of the system and for the interaction between the electron and the atomic or molecular constituents of the system. Some applications of the Feynman path-integral formulation to electron–solvent and electron–cluster interactions (in water) rest on oversimplified electron–solvent potentials[58–60] akin to those used in the semicontinuum models,[42–48] while more refined electron–water pseudopotentials have been recently presented,[59(b),61–64] in this context.

In this paper, and in the following one, we focus on excess electron states in water clusters. While several interaction potentials are available for the intra- and intermolecular interactions in water,[65] the construction of reliable interaction potentials between an electron and a water molecule in its electronic ground state is a more recent development.[61–64] The objective is to develop a theoretical model which will reduce the many-electron problem to a one-electron problem expressed in terms of an effective potential which could be used in the path-integral simulations. In formulating such an approach, the methodology of pseudopotential theory, developed in the context of the electronic strucure of condensed phases,[66] and in certain quantum-chemical calculations,[67–69] is most valuable. At this junction, we remark that

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studies of excess electron states in clusters provide a most convenient starting point for the construction and testing of such an effective potential, since by varying the cluster size one passes from the molecular to the condensed phase regimes. Moreover, an assessment of the quality of the constructed potential can be made via comparisons to the available many-electron cluster quantum-chemical calculaions.[50] Guided by the above ideas we describe in this paper the construction of a pseudopotential[63,64] for electron interaction with a water molecule in its ground electronic state, which we then employ in studies of electron attachment and localization in small water clusters (see paper II[70]). It is of interest that the pseudopotential which we constructed and used in our simulations,[63,64,70] is quantitatively similar to that developed using a different approach by Schnitker and Rossky[61] and employed by these authors in path-integral simulations[62] of electron solvation in bulk water. Following the description of the potential in Sec. II, we summarize in Sec. III the classical intra- and intermolecular potential[71,72] which we used in our simulations.[70]

II. ELECTRON–WATER MOLECULE PSEUDOPOTENTIAL

The formulation of the effective electron–molecule potential is simplified by considering the electorn as a probe of the target molecule, (similar to the approach used in electron–molecule scattering theory). In the spirit of density-functional theory,[73] it is convenient to separate the potential experienced by the electron into the Coulomb ($V_{\rm Coul}$), polarization (V_p), exclusion (V_e), and exchange (V_x) contributions,

$$V(\mathbf{r}_e,\mathbf{R}_0,\mathbf{R}_1,\mathbf{R}_2) = V_{\rm Coul} + V_p + V_e + V_x\,, \tag{1}$$

where $\mathbf{r}_e$ is the electron position and $\mathbf{R}_0$, $\mathbf{R}_1$, and $\mathbf{R}_2$ are the positions of the oxygen and two hydrogens of the water molecule, respectively. Contours of the potential in the plane of the molecule with the oxygen at the origin are shown in Fig. 1. A maximum magnitude of 0.1 hartree was imposed in generating all of the potential contour plots shown in this paper, this results in the jagged ± 0.1 hartree contour lines.

A. The Coulomb potential

The Coulomb contribution, which in the context of scattering theory is often referred to as the static potential,[68,69] consists of the interaction of the electron with positive point charges, $q_1 = q_2 = 0.6\,e$, located on the hydrogens (located at $\mathbf{R}_1$ and $\mathbf{R}_2$) and with a negative point charge, $q_3 = -1.2e$, located at $\mathbf{R}_3 = \mathbf{R}_0 + (\mathbf{R}_1 + \mathbf{R}_2 - 2\mathbf{R}_0)\delta$, where $\delta = 0.221\,837\,56$. The values of q_i ($i = 1$–3) and δ are those used in the RWK2-M model intermolecular potential for water[71,72] (see Sec. II B) which were chosen to yield accurate values for the dipole and quadrupole moments of H_2O. Thus, $V_{\rm Coul}$ is given by

$$V_{\rm Coul}(\mathbf{r}_e,\mathbf{R}_0,\mathbf{R}_1,\mathbf{R}_2) = -\sum_{j=1}^{3} q_j e/\max(|\mathbf{r}_e - \mathbf{R}_j|,R_{cc})\,, \tag{2}$$

where the cutoff value $R_{cc} = 0.5\,a_0$ is introduced for computational convenience.

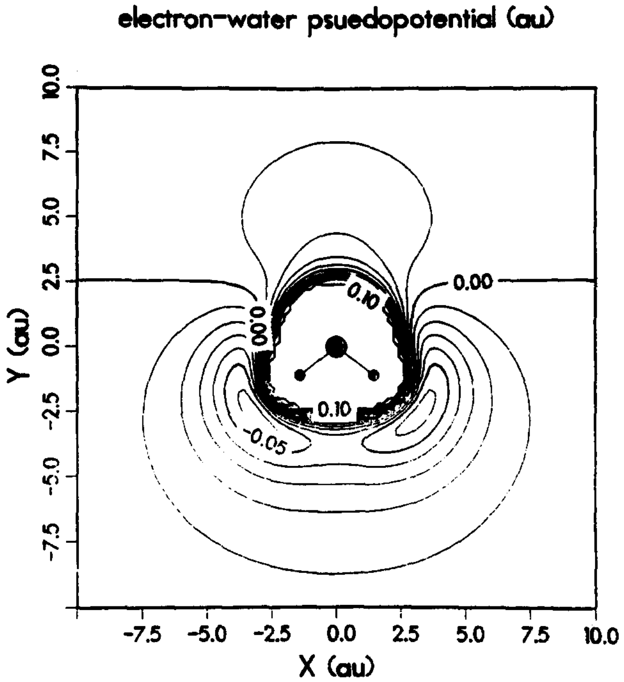

FIG. 1. Contours of e–H_2O total interaction potential in the plane XY of the molecule. The oxygen atom is at the origin and the hydrogens at ($-1.430\,43$, $-1.107\,16$, 0.0) and (1.430 43, $-1.107\,16$, 0.0). The minima of the potential in the vicinity of the hydrogens are -0.064 hartree. The increment Δ between neighboring contours is 0.01 hartree. (1 hartree = 27.212 eV). Note the repulsive barrier when approaching the oxygen from the backside of the molecule. Distance in units of the bohr radius a_0. A maximum magnitude of 0.1 hartree was imposed in generating all of the potential contour plots shown in this paper, this results in the jagged ± 0.1 hartree contour lines.

Contours of the Coulomb potential in the plane of the molecule with the oxygen atom located at the origin are shown in Fig. 2. A detailed plot of the contribution of the Coulomb potential, as well as the other terms, to the pseudopotential [Eq. (1)] vs distance along one of the O–H bonds, is shown in Fig. 3 (the hydrogen atom is located at $1.8\,a_0$ and the oxygen at the origin. Negative values on the distance axis correspond to approach of the electron along the O–H bond from the other side of the oxygen atom). As seen approach towards the hydrogn from the H side yields an attractive Coulomb interaction which turns into a sharp repulsion as the oxygen is approached. The Coulomb interaction on the other side of the oxygen atom is purely repulsive.

B. The polarization potential

The polarization potential V_p consists in principle of an adiabatic polarization potential and a correction due to nonadiabatic effects.[69] Since the latter has not as yet been determined[69] we limit ourself to the adiabatic contribution. A calculation scheme for this term was suggested by Douglass *et al.*[69] It consists of first performing a matrix Hartree–Fock self-consistent-field molecular orbital calculation for a given molecular geometry, which yields a molecular wave function ψ_0 and a corresponding energy E_0. Next a negative unit test charge is added at a positive $\mathbf{r}_e$. The associated perturbation Hamiltonian is given by

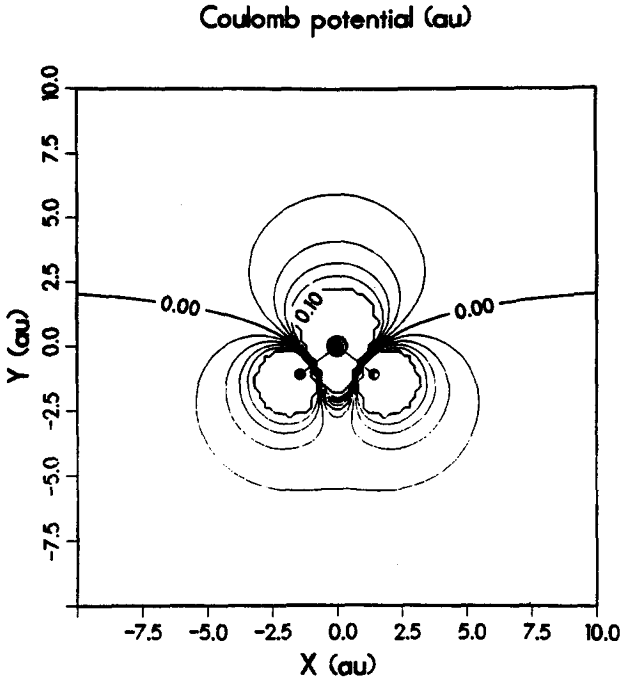

FIG. 2. Contours in the plane of the molecule of the Coulomb contribution [Eq. (2)] to the e–H_2O interaction potential. The potential is attractive (negative) on the side of the hydrogens and repulsive (positive) on the side of the oxygen. The increment between neighboring contours is 0.02. For further details see caption to Fig. 1.

$$H_1(\mathbf{r}_e) = \sum_i \frac{1}{|\mathbf{r}_i - \mathbf{r}_e|} - \sum_\alpha \frac{Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}_e|}, \qquad (3)$$

where $\mathbf{r}_i$ are the molecular electrons, and $Z_\alpha, \mathbf{R}_\alpha$ are the molecular nuclear charges and positions, respectively. The energy to first order in H_1 (H_0 being the unperturbed molecular Hamiltonian), evaluated for the unrelaxed charge distribution ψ_0, is given by

$$E_1(\mathbf{r}_e) = \langle \psi_0 | H_0 + H_1(\mathbf{r}_e) | \psi_0 \rangle . \qquad (4)$$

Additional iterations, to convergence, give the adiabatically perturbed wave function $\psi_1(\mathbf{r}_e;\{\mathbf{r}_i\})$, and the final energy of the system is

$$E_2(\mathbf{r}_e) = \langle \psi_1(\mathbf{r}_e;\{\mathbf{r}_i\}) | H_0 + H_1(\mathbf{r}_e) | \psi_1(\mathbf{r}_e;\{\mathbf{r}_i\}) \rangle . \qquad (5)$$

Finally, the adiabatic polarization potential V_p is given by

$$V_p(\mathbf{r}_e) = E_2(\mathbf{r}_e) - E_1(\mathbf{r}_e) . \qquad (6)$$

The molecular polarizability is related to V_p by the asymptotic relationship

$$\alpha(r_e) = -2 \lim_{r_e \to \infty} r_e^4(\mathbf{r}_e) . \qquad (7)$$

In our calculations we have fitted the adiabatic polarization potential for H_2O calculated by Douglas *et al.*[69] for several directions from which the test electron approaches the molecule, by the expression

$$V_p(\mathbf{r},\mathbf{R}_0) = -0.5\, \alpha e^2/(|\mathbf{r}_e - \mathbf{R}_0|^2 + R_p^2)^2 , \qquad (8)$$

where $R_p = 1.6\, a_0$, and $\alpha = 9.7446$ a.u. is the spherical polarizability of the water molecule.

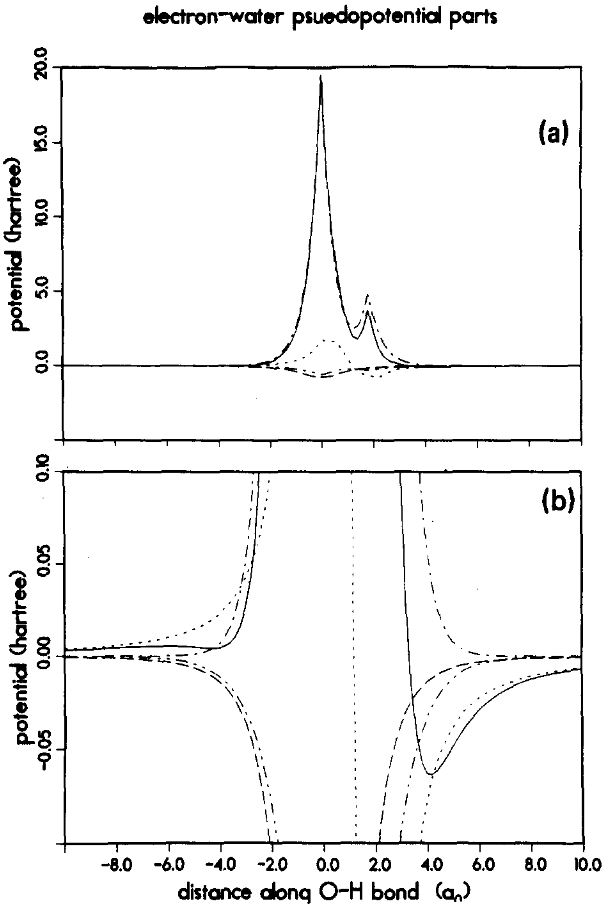

FIG. 3. Linear plots of the total e–H_2O interaction potential [Eq. (1)] and contributions to it vs distance, along one of the O–H bonds. For the molecular coordinates see caption to Fig. 1. In (b) an expanded view is given of the (−0.1,0.1) region of the potential shown in (a). Total potential, solid line; Coulomb contribution, short dashed line; polarization contribution, long dashed line; exclusion contribution, long–short–long dashed line; exchange contribution, long–short–short–long dashed line. Potentials in units of hartree and distance in units of the bohr radius a_0. Note the dominance of the exclusion contribution at short distance from the molecule and the delicate balance between the various contributions at longer distances.

Contours of the polarization potential in the plane of the molecule are shown in Fig. 4, and vs distance along one of the O–H bonds in Fig. 3. Note the attractive long-range nature of the polarization contribution.

C. The exclusion potential

The origin of this contribution is the effect of the Pauli exclusion principle.[67,74] Such a contribution was proposed by Gombas[75,67] within the context of the Thomas–Fermi statistical theory. In the language of pseudopotential theory, it accounts for the orthogonality constraint between the excess electron wave function and the valence molecular electronic orbitals. Expressed differently it represents the enhancement of the kinetic energy of the excess electron, due to the orthogonality requirement.[67,74] Since the excess electron binding to the closed-shell water molecule is small compared to the valence electron binding energies we consider only the s-wave contribution in the expansion of the excess electron wave function. This yields the expression[67,74]

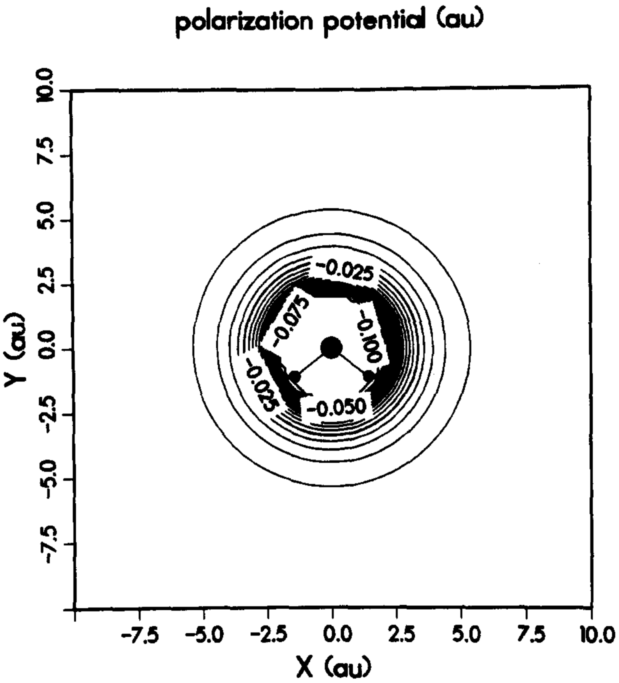

FIG. 4. Contours, in the plane of the molecule, of the polarization contribution [Eq. (8)] to the e–H_2O interaction potential. $\Delta = 0.005$ hartree. For further details see the caption to Fig. 1.

$$V_e(\mathbf{r}_e,\mathbf{R}_0,\mathbf{R}_1,\mathbf{R}_2) = 0.5\, e^2 a_0 (3\pi^2\rho)^{2/3}, \tag{9}$$

where ρ is the electron density of the water molecule. In the regions of importance, i.e., accessible by the excess electron, the calculated electron density for the H_2O molecule[76] is adequately approximated by the simple expression (see Fig. 5)

$$\rho(\mathbf{r},\mathbf{R}_0,\mathbf{R}_1,\mathbf{R}_2) = 8\, a_0^{-3} e^{-3|\mathbf{r}-\mathbf{R}_0|/a_0} + a_0^{-3} \sum_{j=1}^{2} e^{-3|\mathbf{r}-\mathbf{R}_j|/a_0}. \tag{10}$$

The contours of the exclusion potential in the plane of the molecule shown in Fig. 6 and its variation along one of the OH bond demonstrate its repulsive dominance at short range.

D. The exchange potential

The final contribution to the pseudopotential in Eq. (1) is due to exchange which is a consequence of the antisymmetrization of the wave function.[77–80] Rigorously, the exchange potential is nonlocal. However, most of the development of electronic structure and electron–molecule scattering theory rely on local exchange approximations. We will adopt the approach originated by Slater,[77] and model the exchange potential by the expression

$$V_x(\mathbf{r}_e,\mathbf{R}_0,\mathbf{R}_1,\mathbf{R}_2) = -\alpha_x e^2 (3\pi^2\rho)^{1/3}/\pi. \tag{11}$$

The parameter α_x was taken to be $\alpha_x = 0.3$ in order to obtain good agreement between our simulation results and the self-consistent field results of Rao and Kestner[50] for $(H_2O)_8^-$ at a fixed configuration of the water molecules.

As seen from the contours in Fig. 7 and the plots in Fig. 3 (long-double-dash line) the attracive exchange contribution is small. However, in the total intraction potential [see contours in the plane of the molecule, in Fig. 1(a), and solid line in Fig. 3] a delicate balance between the various contributions occurs. Thus, e.g., upon approach along an O–H bond from the hydrogen side the exchange contribution is larger in magnitude than the polarization for distances from the oxygen larger than 3 a_0. While for an approach from the backside of the oxygen atom it is comparable in magnitude to

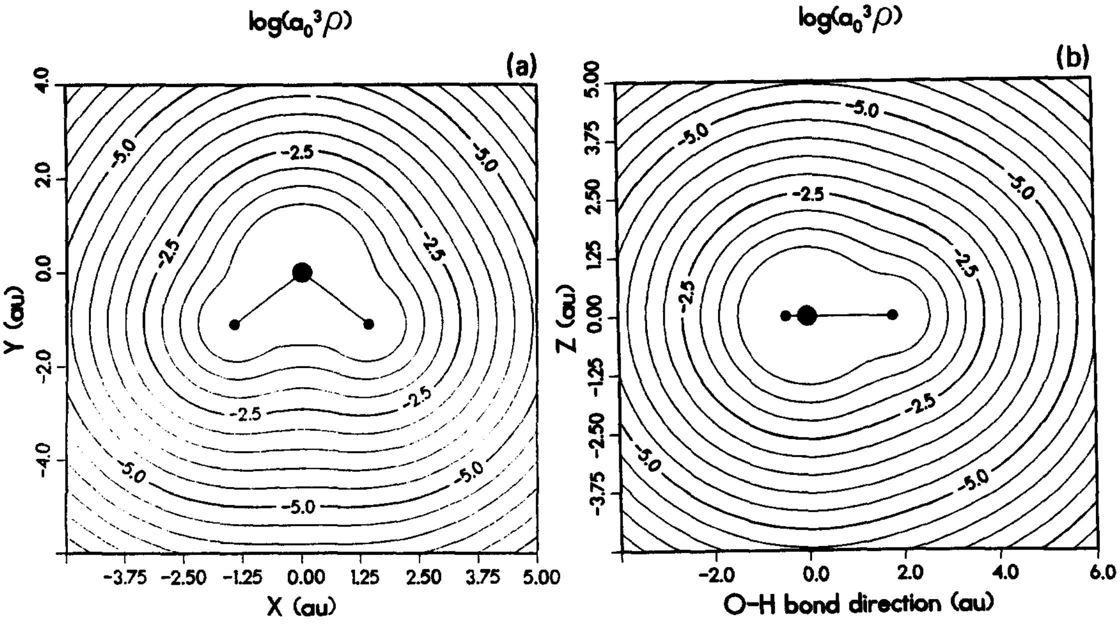

FIG. 5. Contours of the logarithm (base 10) of the water molecule electron charge density ρ as fitted by Eq. (10). Distance in unit of the bohr radius a_0. The oxygen atom is at the origin. In (a) contours in the plane of the molecule and in (b) in a plane containing an O–H bond and normal to the molecular plane.

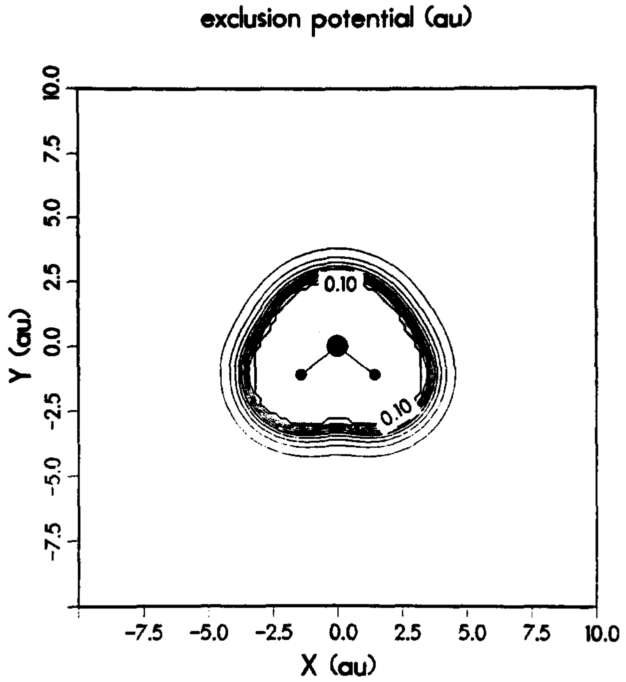

FIG. 6. Contours, in the plane of the molecule, of the exclusion contribution [Eq. (9)] to the e–H_2O interaction potential. $\Delta = 0.01$ hartree and the magnitude decreases from the molecule outwards. For further details see the caption to Fig. 1.

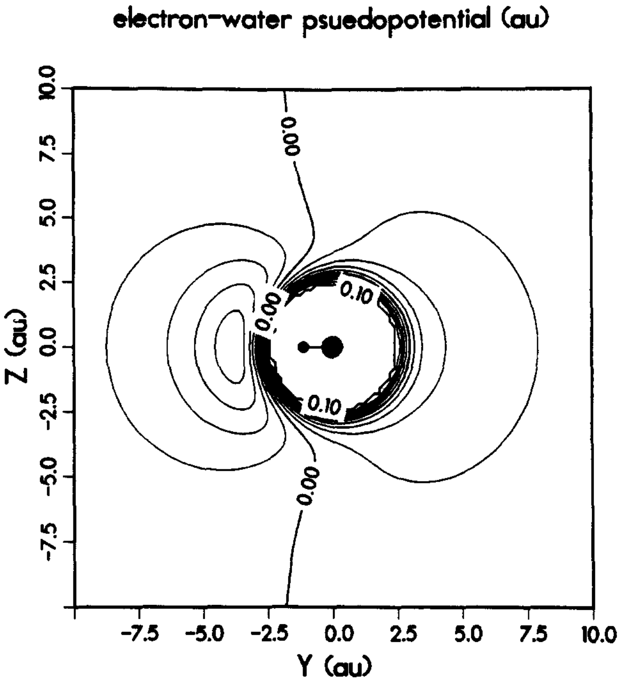

FIG. 8. Contours of total e–H_2O interaction potential [Eq. (1)] in the plane bisecting the H–H distance (ZY) and containing the oxygen. For further details about the molecular coordinates see the caption to Fig. 1. The minimum of the potential on the hydrogens side (negative Y coordinate) is at -0.046 hartree, and the increment between neighboring contours $\Delta = 0.01$ hartree. Distance in unit of the bohr radius a_0.

the polarization potential but is of shorter range. Furthermore, we found that we could not obtain a satisfactory fit to the quantum-chemical cluster calculations[50] when the exchange contribution was omitted.

To complete the characterization of the total potential [Eq. (1)] we exhibit in Figs. 8–10 contours of the potential: (a) in the plane bisecting the H–H distance and containing the oxygen (Fig. 8, the hydrogen are at negative y coordinates); (b) in the plane containing the oxygen and normal to the molecular plane (Fig. 9); (c) in the plane normal to the molecular plane and containing the one of the O–H bonds (Fig. 10).

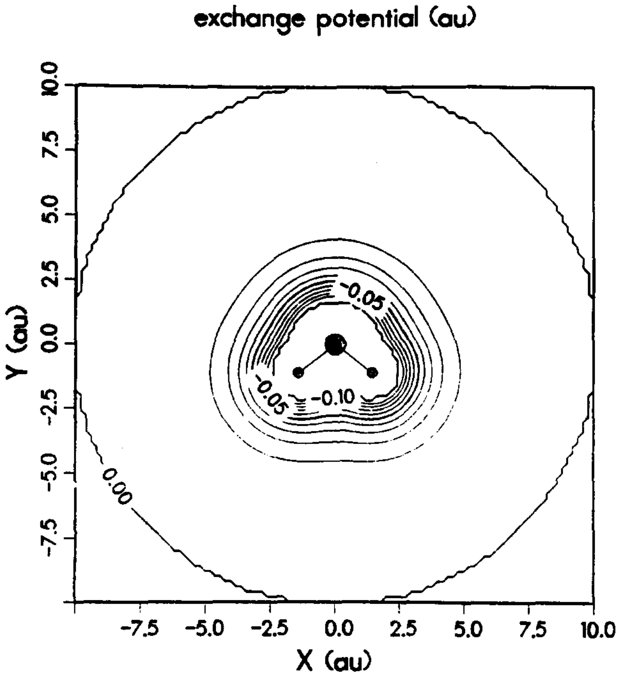

FIG. 7. Contours in the plane of the molecule of the exchange contribution [Eq. (11)] to the e–H_2O interaction potential. $\Delta = 0.01$ hartree. For further details see the caption to Fig. 1.

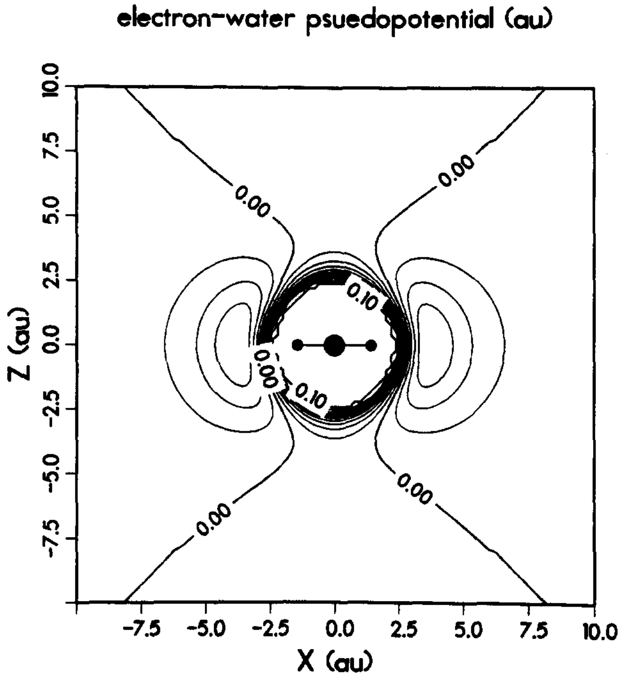

FIG. 9. Contours of the total e–H_2O interaction potential in the plane (ZX) containing the oxygen and normal to the molecular plane (XY). The minima of the potential in the vicinity of the hydrogens are at -0.039 hartree, $\Delta = 0.01$ hartree. For the molecular coordinates see caption to Fig. 1.

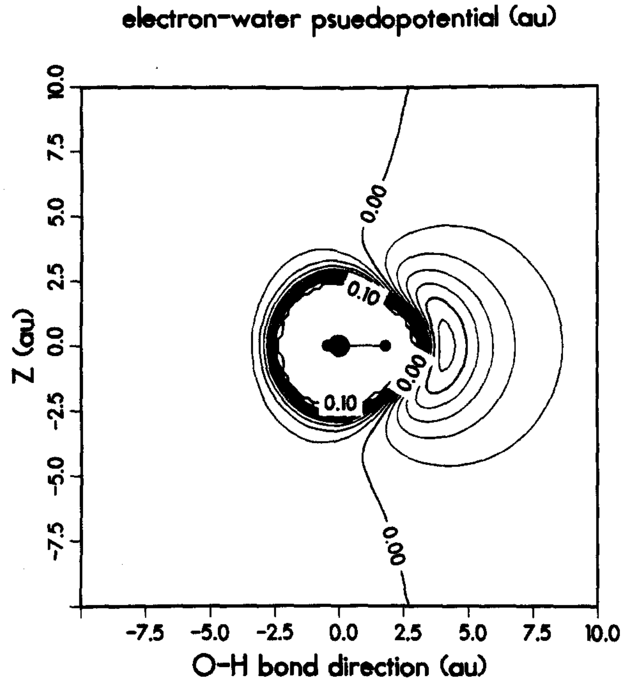

FIG. 10. Contours of the total e–H_2O interaction potential in the plane normal to the molecular plane and containing one of the OH bonds. The minimum of the potential in the vicinity of the hydrogen is at -0.064 hartree. $\Delta = 0.01$ hartree.

In our path-integral calculations (see paper II) we found for the static eight molecule cluster, in the configuration used by Rao and Kestner,[50] a binding energy of -0.0226 hartree (-0.6147 eV) at 158 K (and -0.0230 hartree at 79 K), employing 2048 and 4096 bead particles, respectively (for details see paper II[70]). These values compare well with the corresponding values obtained by the quantum-chemical calculations[50] in which a correction due to the difference between the calculated and observed molecular dipole moments was included. The relative contributions to the potential energy of the electron (with respect to the total) from the various terms in the potential [Eq. (1)] are $V_{\rm Coul}$ (-0.0706), V_p (-0.0272), V_e (0.0529), and V_x (-0.0283).

III. INTER- AND INTRAMOLECULAR POTENTIALS FOR WATER: THE RWK2-M POTENTIALS (REFS. 71 AND 72)

To complete the descriptions of the interaction potentials used in our simulations, we list the RWK2-M inter- and intramolecular potentials[71,72] which we exployed. We repeat here the statement of these potentials since the original publications[71,72] where they were developed contain a number of ambiguities and typographical errors, which when corrected yield the results described in those publications.

In the following $\mathbf{R}_0$ denotes the location of the oxygen atom and $\mathbf{R}_i$ $(i = 1,2)$ the locations of the hydrogens. The potential parameters were chosen to fit known properties of water.

A. Intramolecular potential (Ref. 72)

The intramolecular H_2O potential, which was determined on the basis of a large basis set vibrational calculation to fit 56 vibrational levels for H_2O, D_2O and HDO, is given by

$$\phi^{(1)}(\mathbf{R}_0,\mathbf{R}_1,\mathbf{R}_2) = \sum_{i=1}^{3} D_i[1-\exp(-\alpha_i S_i)]^2, \qquad (12)$$

where

$$S_i = |\mathbf{R}_i - \mathbf{R}_0|\cos\left(\frac{\theta-\theta_{\rm eq}}{2}\right) - R_{\rm eq}, \quad (i = 1,2) \qquad (13)$$

and

$$S_3 = (|\mathbf{R}_1 - \mathbf{R}_0| + |\mathbf{R}_2 - \mathbf{R}_0|)\sin\left(\frac{\theta-\theta_{\rm eq}}{2}\right)/R_{\rm eq},$$
$$\cos\theta = (\mathbf{R}_1 - \mathbf{R}_0)\cdot(\mathbf{R}_2 - \mathbf{R}_0)/$$
$$(|\mathbf{R}_1 - \mathbf{R}_0||\mathbf{R}_2 - \mathbf{R}_0|).$$

$R_{\rm eq} = 1.8088\, a_0$ and $\theta_{\rm eq} = 104.52°$ are the equilibrium O–H bond length and HOH angle, respectively. The values of the parameters are given in Table I.

B. Intermolecular potential (Ref. 71)

The intermolecular potential between two molecules whose nuclear coordinates are denoted collectively by $\{\mathbf{R}\}$ and $\{\mathbf{R}'\}$ is given by

$$\begin{aligned}\phi^{(2)}(\{\mathbf{R}\},\{\mathbf{R}'\} = & \sum_{i,j=1}^{3} C_{ij}(|\mathbf{R}_i - \mathbf{R}_j'|) \\ & + \sum_{i,j=1}^{2} E_H|\mathbf{R}_i - \mathbf{R}_j'|) + E_O(|\mathbf{R}_O - \mathbf{R}_0'|) \\ & + \sum_{i=1}^{2} [M(|\mathbf{R}_0 - \mathbf{R}_i'|) + M(|\mathbf{R}_i - \mathbf{R}_0'|) \\ & + D(|\mathbf{R}_0 - \mathbf{R}_0'|). \qquad (14)\end{aligned}$$

The Coulomb interaction between point charges [q_1

TABLE I. Values of the RWK2-M potential parameters. Energy in a.u. = hartree = 2 Ryd. Length in bohr radius, a_0.

Equation (12)	$D_i(i = 1,2)$	$\alpha_i(i = 1,2)$	D_3	α_3
	0.209 12 a.u.	1.1298 a_0^{-1}	0.157 91 a.u.	0.703 37
Equation (16)	$A_{\rm H}$	$\alpha_{\rm H}$	A_0	α_0
	1.007 7 a.u.	1.7360 a_0^{-1}	5110.7 a.u.	2.6301 a_0^{-1}
Equation (17)	A	α	R_m	
	0.003 066 a.u.	3.895 56 a_0^{-1}	3.0951 a_0	
Equation (20)	C_6	C_8	C_{10}	
	62.437 a.u. a_0^6	1343.7 a.u. a_0^8	50050 a.u. a_0^{10}	

$= q_2 = 0.6$ a.u. and $q_3 = -1.2$ a.u. located at $\mathbf{R}_1,\mathbf{R}_2$ and $\mathbf{R}_3 = \mathbf{R}_0 + 0.221\,837\,56\,(\mathbf{R}_1 + \mathbf{R}_2 - 2\mathbf{R}_0)$, respectively] is given by

$$C_{ij}(R) = q_i q_j / R\,. \tag{15}$$

The exponential repulsion between the nuclei is given by

$$E_s(R) = A_s\, e^{-\alpha_s R}, \quad (s = \mathrm{H,O})\,. \tag{16}$$

The Morse potential between an oxygen atom on one molecule a distance R from a hydrogen atom on another molecule is given by

$$M(R) = A\, e^{-\alpha(|\mathbf{R}-\mathbf{R}_m|)}\left[e^{-\alpha(|\mathbf{R}-\mathbf{R}_m|)} - 2\right]. \tag{17}$$

Finally, the dispersion interaction between oxygens in different molecules separated by a distance R is given by

$$D(R) = -F(R)\{C_6[g_6(R)/R\,]^6 + C_8[g_8(R)/R\,]^8 + C_{10}[g_{10}(R)/R\,]^{10}\}\,, \tag{18}$$

where

$$F(R) = 1 - (cR)^{\beta}\exp(-cR)\,, \tag{19}$$

where $c = 0.948\,35\,a_0^{-1}$, $\beta = 2.326$, and

$$g_n(R) = 1 - \exp\{-[aR/n - bR^2/\sqrt{n}\,]\}\,, \tag{20}$$

where $a = 1.9915\,a_0^{-1}$ and $b = 0.980\,30\,a_0^{-2}$.

In applying this potential surface in our calculations we assume that the various parameters are independent of geometry. Detailed studies[72,81,82] employing this model validate this assumption.

ACKNOWLEDGMENTS

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