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Calculations of the Pseudopotential for the Excess Electron in Water and Methane

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The potentials for excess electrons in cavities of water and methane are analyzed with the use of the pseudopotential theory. The results are consistent with the previous discussions; the excess electron in water can probably be trapped in the cavity and that in methane will be quasifree. In the case of methane, the effect of the molecular coordination on the potential is further discussed by varying the cavity radius.

Key words: Pseudopotentials, calculations of ~ – Excess electrons in water and methane

1. Introduction

In previous papers [1, 2], the behavior of excess electrons in polar and nonpolar media was investigated by using semiempirical and nonempirical Hartree-Fock methods. In those works, the potentials for excess electrons in cavities of water and methane were obtained by taking the stabilization energy of an excess electron as an approximate potential; the former shows that the excess electron in water will be trapped by the potential well in the cavity and the latter shows that the excess electron in methane will be quasifree.

In the present paper, we will analyze the potentials for excess electrons in cavities of water and methane with the use of the pseudopotential theory [3–8] and try to throw more light on the electron-trap interaction.

2. Potentials

Firstly, it is assumed that molecules surrounding the cavity do not interact and that the potential V for an excess electron is the sum of potentials due to these independent molecules:

$$V=\sum_n v^n \tag{1}$$

where v^n denotes the potential of nth molecule and the summation runs over all surrounding molecules. Secondly, it is assumed that no distortion of molecules is

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induced by the interaction with an excess electron; that is, the discussion will be carried out in the framework of the first-order perturbation theory.

Then, according to the pseudopotential theory [3–8], v^n is approximated by a pseudopotential v_{ps}^n of nth molecule[1]:

$$v^n = v_{ps}^n = v_{\mathrm{HF}}^n + v_R^n \tag{2}$$

$$V = V_{ps} \equiv \textstyle\sum_n v_{ps}^n \qquad V_{\mathrm{HF}} \equiv \sum_n v_{\mathrm{HF}}^n \qquad V_R \equiv \sum_n v_R^n$$

where, in case the molecule has a closed-shell structure with occupied molecular orbitals ψ_i, the Hartree-Fock potential v_{HF}^n is given by the nuclear attraction potential (v_{nuc}^n) and the Coulomb ($\mathscr{J}_i^n$) and exchange ($\mathscr{K}_i^n$) operators as follows:

$$v_{\mathrm{HF}}^n = v_{\mathrm{nuc}}^n + \textstyle\sum_i (2\mathscr{J}_i^n - \mathscr{K}_i^n) \tag{3}$$

in which the summation runs over all occupied orbitals, and where v_R^n, a repulsion potential based on the Pauli principle, is defined by [5]:

$$v_R^n |\phi_e\rangle = \textstyle\sum_i |\psi_i^n\rangle\langle\psi_i^n|\mathscr{G}|\phi_e\rangle \tag{4}$$

in which ϕ_e is the smooth pseudowave function of an excess electron and $\mathscr{G}$ is an arbitrary operator. A useful form of $\mathscr{G}$ seems to be $-v_{\mathrm{HF}}^n$ [5, 6]. Taking a plane wave as ϕ_e and making its wave vector negligibly small[2] [6], we can rewrite v_{ps}^n as:

$$v_{ps}^n = v_{\mathrm{HF}}^n - \textstyle\sum_i |\psi_i^n\rangle\langle\psi_i^n|v_{\mathrm{HF}}^n\rangle\,. \tag{5}$$

Since the exchange potential will usually small compared with the Coulomb potential, we will neglect it in the calculation of v_{HF}^n (this approximation will be examined in Sect. 4). Then, v_{HF}^n becomes the electrostatic potential[3] [9–12]. On the other hand, since v_R^n will be of short range, so far as v_R^n near the cavity center is discussed, it may be permitted to neglect the contribution from the atoms except the inside hydrogen atoms, that is, to replace the surrounding molecules by only the inside hydrogen atoms with the electron density in their original molecules. This simplification makes it quite easy to calculate v_R^n.

3. Traps and SCF Wave Functions

In both cases of water and methane, the trap is assumed to be formed by four molecules coordinating one of OH or CH bonds toward the cavity center respectively (Fig. 1). The distance from the oxygen atom to the center is set at 2.9200 Å according to the X-ray diffraction experiments [13, 14] and the outside hydrogen atoms are placed at the nearest points to the X-Yplane [1]. The distance from the carbon atom to the center is set at 2.0[4] and 2.5 Å, the former of which

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[1] Following the second assumption, the effect of the core polarization [6] is not included.

[2] In case a localized state of an excess electron is considered taking 1s atomic orbital as ϕ_e [1], Eq. (5) is given by making its orbital exponent negligibly small.

[3] $-v_{\mathrm{HF}}^n$ is frequently used for the studies on the sites of protonation and reactions with electrophilic reagents. For example, see Ref. [12].

[4] The value of 2.0 Å seems to give the most stable anion state; see Ref. [2].

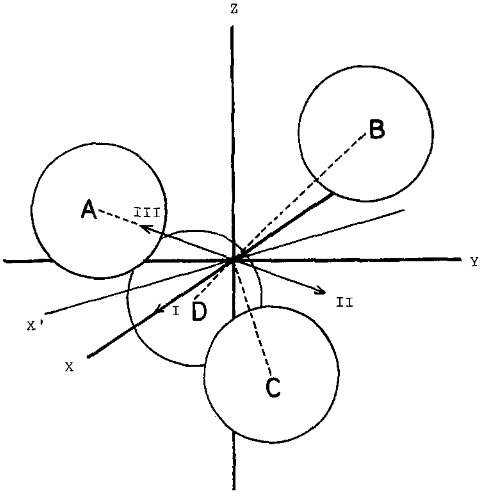

Fig. 1. Four molecules, A, B, C, and D, in a tetrahedral array; one of OH or CH bonds of each molecule points toward the cavity center. X' axis lies on X-Y plane and intersects X axis with a 45° angle. In the case of water, two molecules, A and B, are on X'-Z plane and four outside hydrogen atoms are placed at the nearest points to X-Y plane. In the case of methane, two CH bonds of molecule A (or B) are on X'-Z plane. I indicates the direction along X axis and II and III indicate two opposite directions along the line combining the oxygen (or carbon) atom and the cavity center

is a rough estimation based on the structure of solid methane [15], and the outside hydrogen atoms are placed so that this molecular aggregation may have Td-symmetry[5].

SCF wave functions of water and methane molecules are obtained by using a minimal basis set composed of the Slater-type orbitals with the standard exponents [16]; each orbital is given by a least-squares representation [17] of a sum of three Gaussian-type orbitals.

4. Results and Discussion

4.1. Electrostatic Potentials

In Figs. 2 and 3, the electrostatic potentials in cavities of water and methane are drawn in a.u.; the atoms are projected on X-Z and X'-Z planes. In both cases, there is a flat area near the center and it is clearly shown that the electrostatic potential near a molecule is not much affected by other molecules[6]. The values in the methane cavity are rather lower than those of water, which is mainly brought about by the smallness of the radius of the methane cavity. However, the potential in methane is steeper in direction II than that in water.

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[5] In Ref. [2], the whole system is not accurately in Td-symmetry.

[6] For example, compare the present result for the water cavity with the electrostatic potential (for a proton) of an isolated water molecule in Ref. [18].

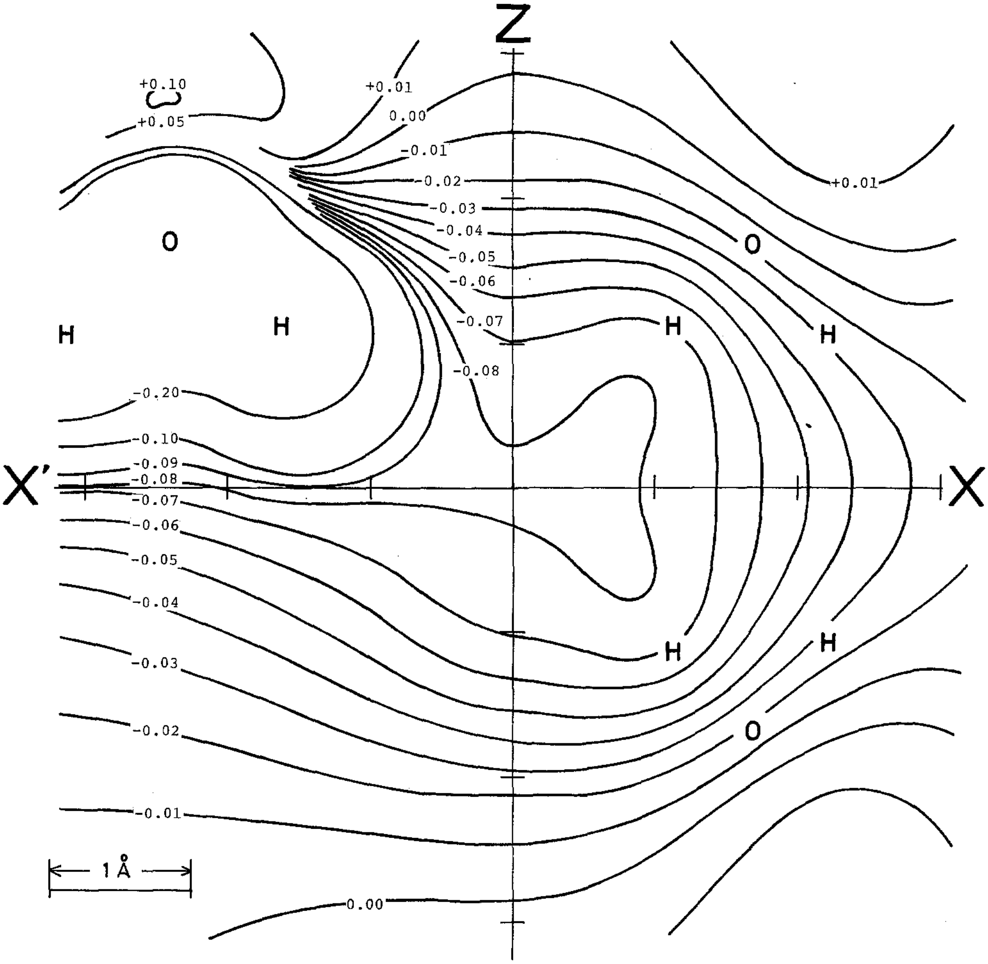

Fig. 2. The electrostatic potential in the case of water (in a.u.)

4.2. The Effect of V_R

By using the approximations described in Sect. 2, v_R^n is given by:

$$v_R^n = (4 - \tfrac{88}{27} P_H^n)\zeta_H^n \exp(-\zeta_H^n r_H^n) \quad \text{(in a.u.)} \tag{6}$$

in the framework of the minimal basis set; P_H^n is the hydrogen atom population of n-th molecule (0.8219 in water molecule and 0.9400 in methane molecule in the present calculation), and r_H^n is the distance (in a.u.) between an excess electron and the nucleus of the hydrogen atom with 1*s* AO (its orbital exponent $\zeta_H^n = 1.24$ a.u.$^{-1}$).

The results are displayed in Figs. 4–7 where (a) and (b) indicate the curves of V_{HF} and V_{ps}, respectively. In Figs. 5–7, the curves in the right- and left-hand sides show the results in directions II and III, respectively and the broken line shows V_{ps} additionally including the exchange potential of only the inside hydrogen

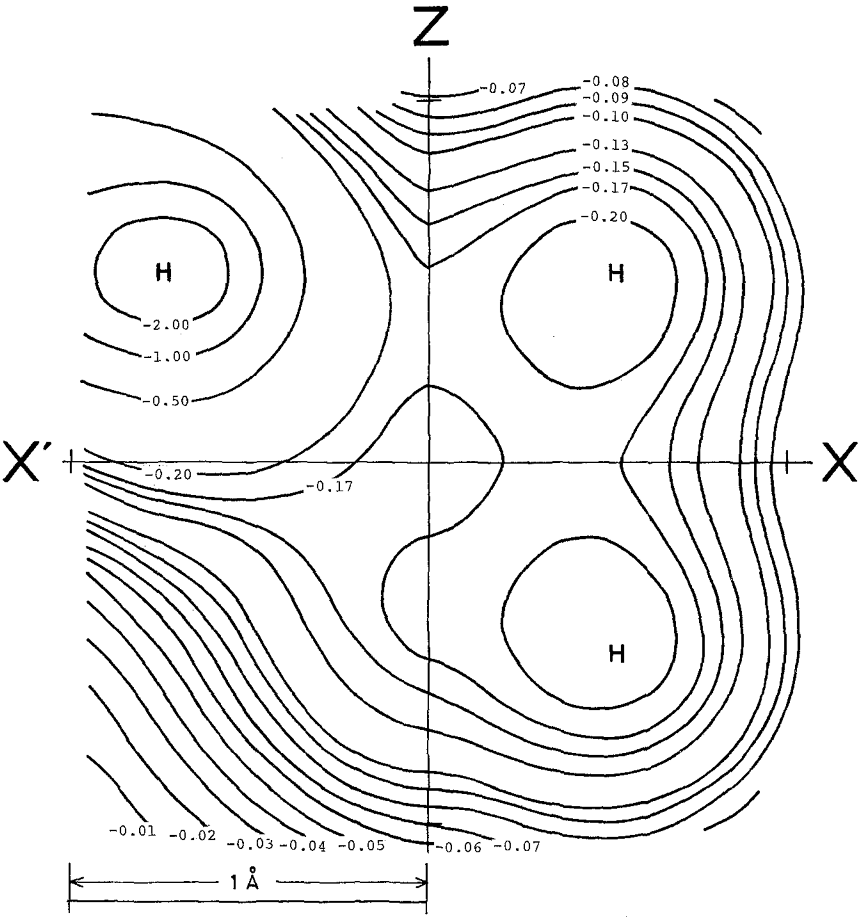

Fig. 3. The electrostatic potential in the case of methane (in a.u.)

atoms. Figs. 4 (direction I) and 5 (directions II and III) are the results of water. Figure 4, which is of course symmetric concerning the cavity center, corresponds to Fig. 6 in a previous paper [1] (therein the value of the potential was all negative and was about -1.0 eV at $X=0$). Curve (a) in Fig. 4 is much elevated by the effect of V_R and, as a result, curve (b) goes positive at $X>0.85$ Å. In the cavity, however, there is surely a potential well (at $X=0$, $V_{ps}=-0.0146$ a.u. $=-0.397$ eV) which resembles the previous one in its shape. In Fig. 5, V_{ps} in direction II becomes rather gentle owing to the rapid decrease of V_R. Though this potential depression will play an indispensable role in the electron trapping, the depth, -0.397 eV, seems to be insufficient to overcome the kinetic energy effect of an excess electron[7] by itself. However, in case the core polarization of the nearest neighboring molecules and the long-range polarization are taken into account [19], the electron

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[7] The ground state of an excess electron in polar solvents is often described by using 1*s* atomic orbital with the orbital exponent near 0.3 a.u.$^{-1}$; for the value of 0.3, the kinetic energy of the electron is about 1.2 eV.

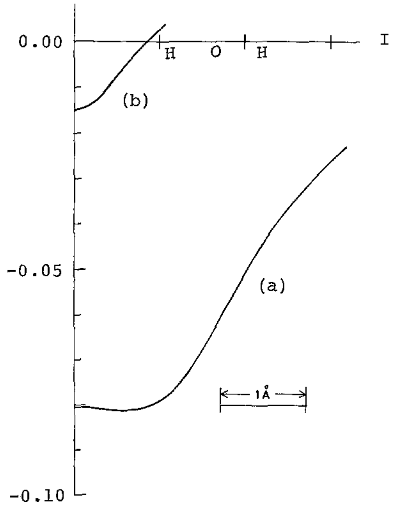

Fig. 4

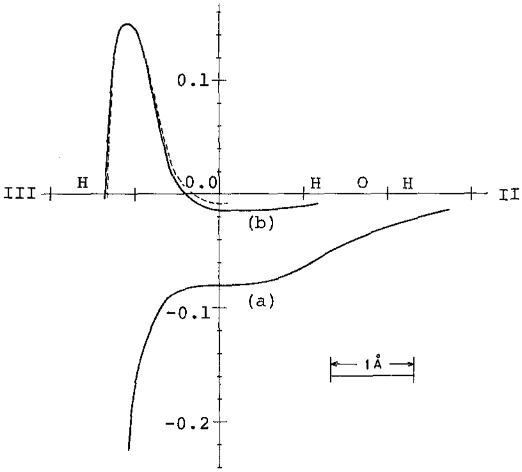

Fig. 5

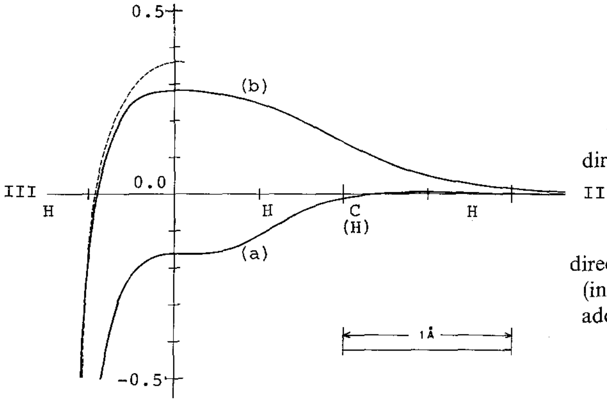

Fig. 6

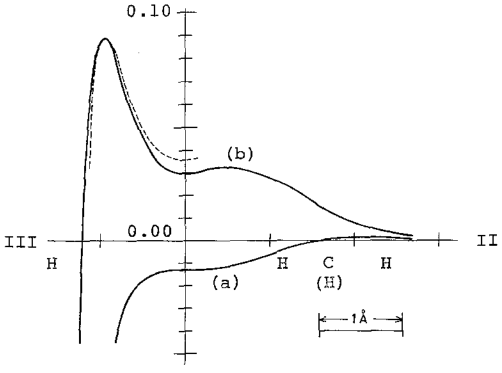

Fig. 7

Fig. 4
The curves of V_{HF} (a) and V_{ps} (b) in direction I in the water cavity (in a.u.)

Fig. 5
The curves of V_{HF} (a) and V_{ps} (b) in directions II and III in the water cavity (in a.u.). The broken line indicates V_{ps} additionally including the effect of the exchange potential of the inside hydrogen atoms

Fig. 6
The curves of V_{HF} (a) and V_{ps} (b) in directions II and III in the methane cavity (in a.u.). The distance between the carbon atom and the center is set at 2.0 Å. The broken line indicates V_{ps} additionally including the effect of the exchange potential of the inside hydrogen atoms

Fig. 7
The curves of V_{HF} (a) and V_{ps} (b) in directions II and III in the methane cavity (in a.u.). The distance between the carbon atom and the center is set at 2.5 Å. The broken line indicates V_{ps} additionally including the effect of the exchange potential of the inside hydrogen atoms

will be bound in the cavity. As previously mentioned [1], the electron moving along direction III encounters at first a potential barrier (with a height of 0.177 a.u. = 4.82 eV in the present calculation) caused by the large repulsion of V_R near the hydrogen atom. The exchange potential is repulsive in the cavity but its effect seems to be trivial.

Fig. 6 shows the results of methane; the distance from the carbon atom to the cavity center is set at 2.0 Å. In this case, the cavity radius is rather small compared with that of water, which causes (1) the deep depression of the electrostatic potential near the center [curve (a)] though it is repulsive in the region $1.16 < r < 2.49$ Å along direction II (r: the distance from the cavity center) and (2) the large repulsion of V_R which makes V_{ps} positive everywhere in the cavity [curve (b)]. It should be noticed that, if V_R and the exchange potential are accurately estimated, V_{ps} in direction III will once ascend toward the outside except in the regions around nuclei. The obvious discrepancy between curve (b) in the right-hand side and the previous curve [2] suggests us that, when the cavity radius is so small, it is indispensable to take into account of the induced polarization, the charge transfer, and so on[8] (the exchange potential seems to be small according to the result of the broken line). In any case, it is sure that, unlike the case of water, an excess electron feels the repulsion potential in the intermolecular region and is quasifree. It will then be worthwhile to clarify the electron-methane molecule potential after an excess electron goes outward from the cavity in liquid methane. Here, we will present the result of the potential in the cavity with a slightly larger radius – the distance from the carbon atom to the cavity center is 2.5 Å – as a datum to consider such a situation. In Fig. 7, it is found that the values of curve (b), in which the exchange potential is relatively small like in Fig. 6, decrease to about a tenth of those in Fig. 6 in the intermolecular region, though V_{ps} is still positive, and that curve (b) has a shallow depression near the center; according to a previous calculation [2], however, such a depression would play only a trivial role in the motion of an excess electron. Furthermore, there appears a peak with a height of 0.098 a.u. = 2.7 eV in curve (b) in direction III. The distance from the carbon atom to the peak is about 1.5 Å and is not noticeably different from the scattering length [6] 1.02 Å estimated approximately by Fueki [21]. These results disclose that the expansion of the cavity by only 0.5 Å brings the feature of the potential of an isolated methane molecule into relief in the total potential. From the above discussions, it is anticipated that an excess electron in liquid methane drifts repeating the scattering by a molecule and the transient stay in the fortuitous molecular aggregation [22–25]. The circumstance would be similar in other saturated hydrocarbons.

Thus, by using the pseudopotential theory, the potential in the cavity has been analyzed and the important role of the repulsion potential due to molecular electrons in the vicinity of a molecule has been pointed out. As a matter of course, the short-range part (except the polarization part) in the isotropic model potentials presented by other authors [26, 27] should be regarded as the orientation-averaged result of the anisotropic potential like the present one. The above discussion will help to consider the dynamical motion of electrons in liquids and solids [28].

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[8] Concerning the relation between the pseudowave function and the charge transfer and polarization effects, a discussion is carried out in Ref. [20].

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