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Comparison of quasifree excess electron and positron states in simple molecular fluids: Methane and silane

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The ground-state energy V_0 (relative to vacuum) of quasifree excess electrons and positrons in two simple molecular fluids, namely, methane and silane, is calculated as a function of fluid density n. The calculations are performed within the framework of the Wigner-Seitz approximation for nonpolar fluids, using semiempirical potentials to model the excess electron (positron) -molecule interactions. Values of $V_0(n)$ are found to be negative over the whole range of densities considered (up to the triple points of the two fluids) for both excess electrons and positrons. In the case of quasifree electrons, a pronounced minimum is observed in the variation of V_0 as a function of n, while for positrons V_0 decreases monotonically with increasing n. Such differences in the $V_0(n)$ variations are briefly discussed.

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INTRODUCTION

Positron-matter studies provide a unique insight into the fundamental aspects of the interactions of charged particles with matter in all its forms [1]. One of the most challenging problems concerns the nature of positron states in fluids and solids. In this context, it is interesting to compare, in a first step, the behavior of quasifree excess electrons and positrons in these systems.

A quantity of central interest for describing quasifree electron and positron states in condensed systems is the ground-state energy V_0 (relative to vacuum) of injected particles. In our previous papers, we have studied the dependence of V_0 as a function of fluid density n for quasifree excess electrons and positrons in rare-gas fluids [2,3], and for quasifree excess electrons in fluid methane [4]. In the present work, we extend our studies to the case of two simple molecular fluids, namely, methane (CH_4) and silane (SiH_4). Methane and silane molecules, because of their high degree of symmetry and their electronic similarity to rare gases, can be viewed as interesting links between complicated polyatomic molecular systems and rare-gas materials. Note that SI units are used in this paper unless otherwise specified.

MOLECULAR POTENTIAL

A proper description of the interaction of a charged particle with a molecular fluid requires the choice of an accurate molecular potential. The various terms (static, electron exchange, and correlation) of the molecular potential can be deduced within the framework of the density-functional theory [5] once the electron density of the target molecule is known. Recently, Gianturco, Di Martino, and Jain [6] have used multicenter target wave functions in order to obtain the charge density function $\rho(\mathbf{r})$ in terms of a single-center expansion around the center of mass of the molecule. This charge density is employed to determine the molecular potential $V(\mathbf{r})$, which, for closed-shell molecules such as methane and silane, can be expanded in terms of symmetry-adapted functions belonging to the totally symmetric A_1 irreducible representation of the molecular T_d point group. Since the CH_4 and SiH_4 molecules have no dipole or quadrupole moments, only the spherical term of this expansion is retained.

Electron-molecule interaction

In the case of an incident electron, $V(r)$ is a sum of three spherical terms, namely, the static $V_{\rm st}^{\rm el}(r)$, electron exchange $V_{\rm ex}^{\rm el}(r)$, and correlation $V_{\rm corr}^{\rm el}(r)$ potentials,

$$V(r)=V_{\rm st}^{\rm el}(r)+V_{\rm ex}^{\rm el}(r)+V_{\rm corr}^{\rm el}(r) . \tag{1}$$

$V_{\rm st}^{\rm el}(r)$ describes the Coulombic interaction between the incident electron and the molecule. It is evaluated using the method given by Gianturco and Thompson [7]. $V_{\rm ex}^{\rm el}(r)$ arises from the indistinguishability of the incident electron from electrons of the target molecule and is approximated by the Hara free-electron-gas-exchange model potential [8]

$$V_{\rm ex}^{\rm el}(r)=-\frac{e^2k_F(r)}{2\pi^2\varepsilon_0}\left[\frac{1}{2}+\frac{1-\eta(r)^2}{4\eta(r)}\ln\left|\frac{1+\eta(r)}{1-\eta(r)}\right|\right] , \tag{2}$$

where $k_F(r)=[3\pi^2\rho(r)]^{1/3}$, $\eta(r)=[k^2+(2m_0I/\hbar^2)+k_F^2]^{1/2}/k_F$, e is the electronic charge, ε_0 is the permittivity of the vacuum, k is the magnitude of the incident electron wave vector, m_0 is the free-electron mass, I is the first ionization potential of the molecule, and $\hbar$ is the Planck constant divided by 2π. Finally, $V_{\rm corr}^{\rm el}(r)$ takes into account target polarization effects induced by the incident electron, and has the following semiempirical analytical form [9,10]:

$$V_{\rm corr}^{\rm el}(r)=-\frac{e^2\alpha}{2(4\pi\varepsilon_0)^2r^4}\left\{1-\exp\left[-\frac{r}{r_c}\right]\right\}^6 , \tag{3}$$

where α is the polarizability of the target molecule and r_c is a cutoff parameter to be chosen by fitting the calculated total-elastic cross sections at very low energies to experiment. The values of I, r_c, and α used in this calculation are reported in Table I. In this table, we also give the values of the electron scattering length calculated with the potential $V(r)$ of Eqs. (1)–(3).

TABLE I. Values of the ionization potential I, polarizability α, molecular hard-sphere diameter σ, cutoff radius r_c, and crossing-point radius $r_{\rm cr}$ used in this work. SL denotes the scattering length calculated by the partial-wave expansion method [11] with the molecular potential $V(r)$ described in the text.[a] α is given both in atomic units (a.u.) and in SI units (C m^2/V). a_0 is the Bohr radius.

	CH_4	SiH_4
I (eV)	12.98[b]	11.8[c]
α (a.u.)	17.5[d]	30.4[e]
α (10^{-41} C m^2 /V)	28.9	50.1
σ (units of a_0)	6.90[f]	7.72[g]
r_c (units of a_0) (electron)	0.88	1.023
$r_{\rm cr}$ (units of a_0) (positron)	2.41	2.796
SL (units of a_0) (electron)	-2.51	-4.28
SL (units of a_0) (positron)	-13.0	-11.2

[a] Cross sections of electron-molecule collisions at thermal energies are determined by the scattering length. Although the SL values reported here are not used in the present $V_0(n)$ calculations, they offer reference values in regard to the quality of the molecular potentials employed in this work. The SL values are also useful in analytical models which describe the conduction-band energy minimum in the limit of low fluid densities [12].

[b] Reference [13].

[c] Reference [14].

[d] Reference [10].

[e] Reference [15].

[f] Reference [16].

[g] Reference [17].

Positron-molecule interaction

The interaction of the positron with a molecule is different from that of the electron. Positrons differ from electrons by the sign of their electric charge, but there is also a difference due to the fact that the exchange part of the interaction potential is not present for the case of positron scattering [18].

In this paper, we describe the positron-molecule interaction by means of a potential $V(r)$ composed of two terms, namely, the static potential $V_{\rm st}^{\rm pos}(r)$, which is equal to $-V_{\rm st}^{\rm el}(r)$, and the correlation potential $V_{\rm corr}^{\rm pos}(r)$, which takes into account the effects of target polarization induced by the positron. These effects are very difficult to describe exactly for positron-molecule systems. Arponen and Pajanne [19] have developed a method to solve the problem of a light charged impurity (a positron) in a homogeneous electron gas. Boroński and Nieminen [20] have parametrized the numerical results of these authors [19] for the electron-positron correlation energy $\varepsilon_{\rm corr}(r_s)$ over the whole range of the electron-density parameter r_s, defined as $4\pi r_s^3/3=1/\rho(r)$. The correlation potential, defined as the functional derivative of $\varepsilon_{\rm corr}(r_s)$ with respect to the target undistorted electron density $\rho(r)$ [5], is then calculated from the equation

$$V_{\rm corr}^{\rm pos}(r)=\left[1-\frac{1}{3}r_s\frac{d}{dr_s}\right]\varepsilon_{\rm corr}(r_s) . \tag{4}$$

Using the Boroński-Nieminen interpolation formulas, the analytic expression for $V_{\rm corr}^{\rm pos}(r)$, in the whole range of r_s, is given by [21]

$$2V_{\rm corr}^{\rm pos}(r)=\frac{e^2}{4\pi\varepsilon_0 a_0}\times\begin{cases}\dfrac{-1.82}{\sqrt{r_a}}+[0.051\ln(r_a)-0.115]\ln(r_a)+1.167 , & r_s\le 0.302a_0\\[2ex] -0.92305-\dfrac{0.09098}{r_a^2} , & 0.302a_0\le r_s\le 0.56a_0\\[2ex] -\dfrac{8.7674r_a}{(r_a+2.5)^3}+\dfrac{-13.151+0.9552r_a}{(r_a+2.5)^2}+\dfrac{2.8655}{(r_a+2.5)}-0.6298 , & 0.56a_0\le r_s\le r_{\rm cr} ,\end{cases} \tag{5}$$

where $r_a=r_s/a_0$, and a_0 is the Bohr radius. At large distances, as for the case of electron-molecule systems, the correlation potential is replaced by the correct asymptotic form of the polarization potential, that is,

$$V_{\rm corr}^{\rm pos}(r)=-\frac{e^2\alpha}{2(4\pi\varepsilon_0)^2r^4} , \quad r\ge r_{\rm cr} , \tag{6}$$

where $r_{\rm cr}$ is the crossing-point radius corresponding to the smallest distance where the short- and long-range parts of $V_{\rm corr}^{\rm pos}(r)$ cross each other. The values of $r_{\rm cr}$ used in this calculation are given in Table I. We also present in this table the calculated values of the positron scattering length for both CH_4 and SiH_4.

INCIDENT-PARTICLE–FLUID INTERACTION

The problem of modeling the interaction potential of an incident particle (electron or positron) with a fluid is a complicated one owing to the many-body nature of the interaction. In our previous papers [2–4], the incident-particle–fluid interaction has been described within the framework of the Wigner-Seitz (WS) model [22] for nonpolar fluids. It should be emphasized that this model has been remarkably successful for calculating the ground-state energy $V_0(n)$ of excess electrons in fluid rare gases and methane. In the present paper, we also apply this concept to describe the electron (positron) -fluid interactions in methane and silane.

In the WS model of a nonpolar fluid, each molecule in the fluid is replaced by an equivalent molecular sphere of radius r_{WS}, defined by

$$\frac{4\pi}{3} r_{\mathrm{WS}}^3 = \frac{1}{n} , \tag{7}$$

where n is the fluid number density. The fluid structure is approximated by an average lattice structure with translational symmetry. In the sphere, the short-range electron (positron) -molecule interaction is described by the molecular potential $V(r)$ as presented in the preceding section. The effect of the fluid mainly occurs through the many-body screening of the long-range electron (positron) -molecule polarization interactions. The potential is assumed spherically symmetric, which, when combined with the average translational symmetry condition, amounts to neglecting fluctuations in the fluid and considering an ensemble-average potential acting on the incident particle [22,23].

At a point $\mathbf{r}$ in the WS sphere around a molecule located at the origin, the total potential $U_{\mathrm{WS}}(r)$ seen by the electron or the positron can be expressed as the sum of the potential $V(r)$ due to the molecule at the origin and of the mean potential produced by the molecules lying outside the sphere [2],

$$U_{\mathrm{WS}}(r) = V(r) + n \int V(|\mathbf{r}-\mathbf{r}'|) F(|\mathbf{r}-\mathbf{r}'|) g(r') d\mathbf{r}' . \tag{8}$$

Here, $F(r)$ is a screening function that accounts for the polarization of the surrounding molecules in the fluid due to the presence of the excess electron or the positron. It is approximated by [23]

$$F(r) = \begin{cases} 1 , & r \leq r_{\mathrm{WS}} \\ \left[1 + \dfrac{2\alpha n}{3\varepsilon_0} \right]^{-1} , & r > r_{\mathrm{WS}} . \end{cases} \tag{9}$$

The integration in Eq. (8) is over all the space with the condition that the incident particle is inside only one WS sphere at a time, that is, $|\mathbf{r}-\mathbf{r}'| > r_{\mathrm{WS}}$. The molecule-molecule pair-correlation function $g(r)$ is obtained by solving the Percus-Yevick equation [24] for a hard-sphere fluid model [25] with a molecular hard-sphere diameter σ given in Table I.

Using the interaction potential $U_{\mathrm{WS}}(r)$ of Eq. (8), the ground-state energy V_0 of quasifree excess electrons and positrons is determined by numerically solving the Schrödinger equation for the lowest energy. This is done by subjecting the ground-state electron (positron) wave function $\Psi_0(r)$ to the WS periodic boundary condition $d\Psi_0(r)/dr = 0$ at $r = r_{\mathrm{WS}}$, and by requiring $\Psi_0(r)$ to be regular at the origin.

RESULTS AND DISCUSSION

The results of our $V_0(n)$ calculations for quasifree excess electrons in fluid methane and silane are shown in Fig. 1, along with the experimental data of Asaf, Reininger, and Steinberger [26] and Tauchert, Jungblut, and Schmidt [27] for methane. As we can see, the energy of the lowest electronic state (that is, the conduction-band minimum energy) is negative (relative to vacuum) for both fluids over the whole density range considered. V_0 reaches a minimum value of -0.36 eV for methane and -0.40 eV for silane at the liquid densities of 1.12×10^{22} and 0.74×10^{22} cm^{-3}, respectively. Note that even if the $V_0(n)$ minima for both fluids have roughly the same value, the density dependence of V_0 is more pronounced in the case of silane. Our results are found to reproduce very well the experimental V_0 values for methane. Unfortunately, V_0 measurements as a function of density are not available for silane.

For comparison, we present in Fig. 2 the density dependence of the ground-state energy V_0 calculated for quasifree positrons in the same two fluids. Again, the conduction-band minimum energy is negative (relative to vacuum). However, in contrast to what is observed for excess electrons (Fig. 1), V_0 decreases monotonically with increasing n without showing any minimum for all the densities considered up to the triple points. The $V_0(n)$ variations for both fluids are very similar, although the curve for silane shows a slightly more pronounced curvature. Note that there are no experimental data of V_0 with which to compare our results.

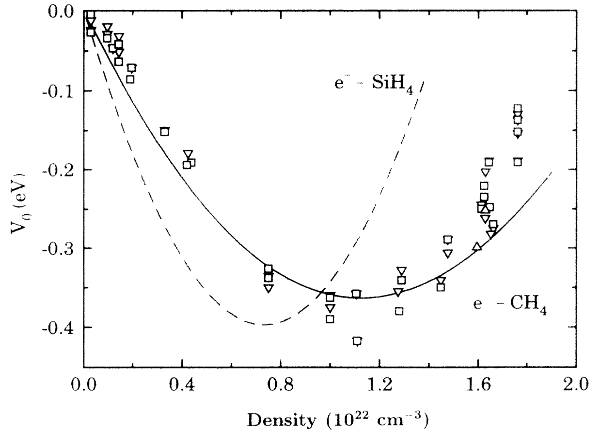

FIG. 1. Energy V_0 (relative to vacuum) of the bottom of the conduction band for quasifree excess electrons in methane (solid line) and silane (dashed line) calculated as a function of fluid density n up to the triple points of the two fluids (see text). Points are experimental results of $V_0(n)$ for methane obtained by Asaf, Reininger, and Steinberger [26] (∇, □), and by Tauchert, Jungblut, and Schmidt [27] using gold electrodes (△). The densities at the triple points are 1.70×10^{22} cm^{-3} (90.7 K) for methane [28] and 1.33×10^{22} cm^{-3} (88.15 K) for silane [29].

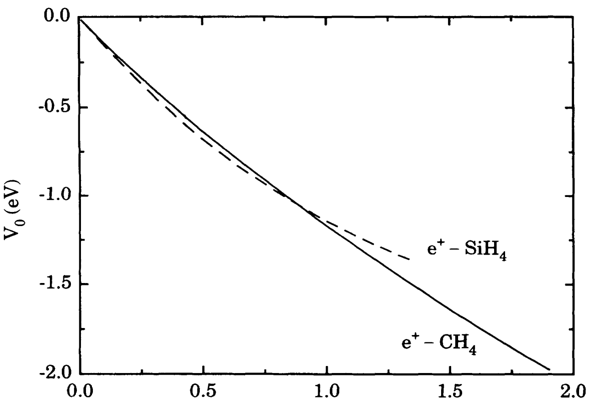

FIG. 2. Energy V_0 (relative to vacuum) of the bottom of the conduction band for quasifree positrons in CH_4 (solid line) and SiH_4 (dashed line) calculated as a function of fluid density n up to the triple points of the two fluids (see text).

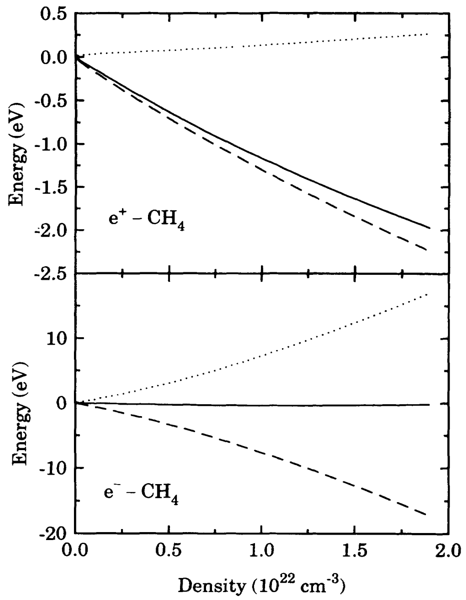

FIG. 4. Density dependence of the mean kinetic (dotted lines), potential (dashed lines), and total (solid lines) energies of quasifree excess electrons and positrons in fluid methane.

A few qualitative remarks can be made about the differences observed in the $V_0(n)$ variations for an excess electron or a positron in the two fluids studied here (Figs. 1 and 2). Let us first consider the case of an excess electron in fluid methane. In the core region, the electron-methane interaction is highly attractive. As a consequence, the electron wave function presents an oscillatory behavior (see Fig. 3) characteristic of a high kinetic energy in that region. This, in turn, limits the volume accessible for the excess electron to the region outside the core. The ratio of the excluded volume to that of the WS sphere increases at higher densities (in other words, the electron is confined to less space) and, consequently, we observe an increase of the mean kinetic and potential energies of the excess electron with increasing density (Fig. 4). The approximate balance of these energies, giving the V_0 values, is easily perturbed by the stronger screening of the long-range electron-molecule polarization interactions as n increases, the overall effect being the appearance of the observed minimum of $V_0(n)$ [30]. The same effect is also expected for quasifree excess electrons in fluid silane. In this case, however, the larger excluded core region (see Fig. 3), along with the larger screening of the polarization forces (the polarizability of SiH_4 is almost twice that of CH_4), lead to a $V_0(n)$ variation much more pronounced than that observed for methane (Fig. 1).

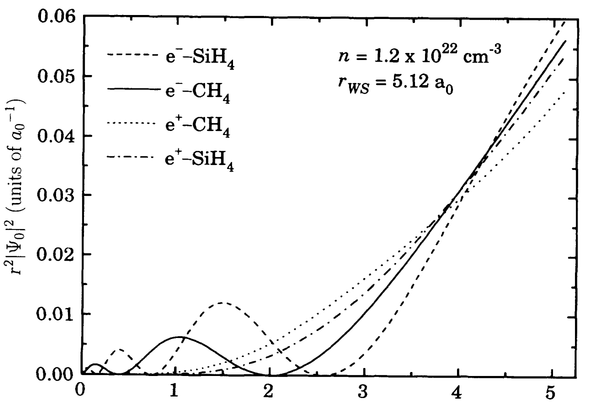

FIG. 3. Comparison of the radial probability distribution function ($r^2|\Psi_0|^2$) for finding the excess electron or the positron in its ground state $\Psi_0(r)$ at a distance r from the center of the WS sphere, for methane and silane at a fluid density $n = 1.2 \times 10^{22}$ cm^{-3} (that is, for a WS sphere radius r_{WS} of $5.12a_0$, where a_0 is the Bohr radius).

The case of a positron injected in fluid methane offers a quite different situation. In fact, the core potential is here highly repulsive. The probability of finding the positron in the core of a molecule is thus very small, but, in contrast to the case of excess electrons, the excluding effect is not associated with an increase in kinetic energy, as can be seen from the smoothness of the positron wave function in Fig. 3. For a positron, the large increase in the mean potential energy with increasing density is not compensated by the slight increase in the mean kinetic energy (see Fig. 4). The V_0 values resulting from these out-of-balance energies are not much influenced by the variation of the screening of the polarization interactions with density. As a consequence, we do not observe any minimum in the $V_0(n)$ curve for positrons in fluid methane. For silane, the situation is similar, although the larger core region and polarizability induce a slightly more pronounced curvature in the variation of V_0 with n (Fig. 2). In closing, we should emphasize the remarkable similarity of the $V_0(n)$ results obtained here for methane and silane with those obtained for the heavy rare-gas systems [2,3,30,31].

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