

Pseudopotentials between an excess electron and a methylene and methyl compound

Abstract

We summarize here the computational details of the pseudopotentials presented in Ref. [1] to describe the interaction between an excess electron and a methylene CH_2 and methyl CH_3 atomic unit, as well as other simulation details. These pseudopotentials produce energies in agreement, within 0.07 eV, with the experimental data on the onset of conduction for ethane and butane fluids, for a large range of atomic densities.

1 Simulation details

The interatomic interaction is simulated using the united atom model [2], in which the CH_2 and CH_3 atomic groups are considered as a whole. The forcefield includes bonded (bond stretch [3], valence angles [2], and dihedrals [4]) and dispersion interactions [2].

A fast Fourier transform (FFT) block Lanczos diagonalization algorithm [5] is used to compute the excess-electron states of static molecules' configurations. This method provides the lowest energy eigenstates for a given 3D potential energy grid. A fixed grid spacing of about 0.7 Å is used in all directions.

The polarization interaction between the electron and the induced dipoles in the system is computed self-consistently using an iteration algorithm (see below). The electron-atom interactions are truncated at the cutoff radius $r_c = 9$ Å, with excess electron energies including the long-range correction discussed in the main manuscript.

2 Pseudopotentials

The potential energy between an excess electron at \mathbf{r} and a system of (united) atoms at $\{\mathbf{R}_i\}$, within the cutoff sphere, can be written as

$$V(\mathbf{r}, \{\mathbf{R}_i\}) = \sum_j V_j^r(|\mathbf{r} - \mathbf{R}_j|) + V^p(\mathbf{r}, \{\mathbf{R}_i\}), \quad (1)$$

where $V_j^r(r)$ is a short-range repulsive pair potential which accounts for the interaction with the static charge distribution as well as exchange and orthogonality of the excess electron with the target atom, and with the explicit form,

$$V^r(r) = \sum_{i=1}^2 A_i \exp(-B_i r). \quad (2)$$

The second term in (1) represents the charge-induced-dipole polarization interaction:

$$V^p(\mathbf{r}, \{\mathbf{R}_i\}) = -\frac{1}{2} \sum_j \mathbf{p}_j \cdot \mathbf{E}_j^{(0)} S_j(|\mathbf{r} - \mathbf{R}_j|), \quad (3)$$

where

$$\mathbf{E}_j^{(0)} = -\frac{e}{4\pi\epsilon_0} \frac{\mathbf{R}_j - \mathbf{r}}{|\mathbf{R}_j - \mathbf{r}|^3} \quad (4)$$

is the direct electric field due to the excess electron, $e = 1.6021766 \times 10^{-19}$ C is the electron elementary charge,

$$\mathbf{p}_j = \alpha_j \mathbf{E}_j \quad (5)$$

the dipole moment of the atom j , α_j the corresponding polarizability tensor, and $S_j(r)$ is a switching function which describes the screening of the electric field due to the charge distribution of the atom as the electron approaches it, going to unity as the electron separates from the target atom. Here we consider the following explicit form for all induced dipoles

$$S(r) = (1 - e^{-r/r_0})^6. \quad (6)$$

In Eq. (5), \mathbf{E}_j is the local electric field at the atom j , which is the superposition of the Coulomb field of the excess electron and the electric fields due to all the other induced dipoles

$$\mathbf{E}_j = \mathbf{E}_j^{(0)} + \sum_{k \neq j} \mathcal{T}_{jk} \cdot \alpha_k \mathbf{E}_k, \quad (7)$$

being $\mathcal{T}_{jk} = (3\hat{\mathbf{r}}_{jk}\hat{\mathbf{r}}_{jk} - \mathbf{1})/r_{jk}^3$. The set of equations (7) is then solved self-consistently using an iterative approach.

2.1 e-CH3 and e-CH2 pseudopotentials

The repulsive potential between the excess electron and the CH₂ and CH₃ units are given [1] by (2) with $A_1 = 8160$ eV and $A_2 = -3590$ eV, combined with the parameters given in table 2.1.

	B_1 (\AA^{-1})	B_2 (\AA^{-1})	δ (\AA)	r_0 (\AA)
CH ₃	4.39	3.91	0.3	0.622
CH ₂	4.67	4.16	0.44	0.622
C-C				0.622

Table 1: Some pseudopotential parameters.

The multicenter polarizabilities obtained in Ref. [6], using quantum *ab initio* calculations, yield the following polarizability tensors (in nF·m²) for the methyl and methylene groups:

$$\alpha_{\text{CH}_3} = \begin{pmatrix} 11.4 & & \\ & 18.3 & \\ & & 18.3 \end{pmatrix}, \quad (8)$$

and

$$\alpha_{\text{CH}_2} = \begin{pmatrix} 4.49 & & \\ & 10.1 & \\ & & 14.7 \end{pmatrix}. \quad (9)$$

In Eq. (8), the x -axis is defined along the C-C bond, whereas in Eq. (9) the x -axis should be taken in the direction defined by the two nearest carbon neighbors in the molecule and the y -axis inside the plane of the carbon nuclei (see Fig. 1). The set of polarizabilities is completed with the polarizability tensor of the bond C-C, which is represented as a polarizable site centered at the middle of the C-C bond with a component $\alpha_{\text{C-C}} = 18.9$ nF·m² in the bond direction, and zero in the perpendicular directions.

The CH₂ and CH₃ polarizable sites are not centered at the carbon atoms [1], but separated from them a small distance δ , given in Table 2.1. In the methyl group, the displacement is outwards the molecule along the C-C bond direction, whereas in the methylene groups it is defined along the y axis defined at Eq. (9).

Since these polarizabilities were calculated neglecting the intramolecular dipole-dipole interaction [6], the direct dipole-dipole interactions between sites closer than a certain distance, taken as $r_{mbmin} = 3$ Å, are ignored.

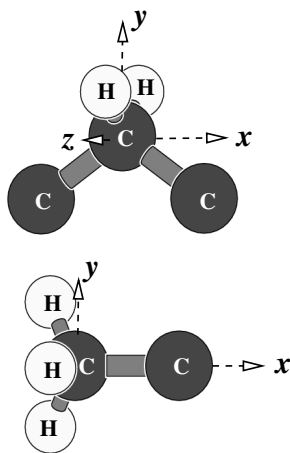


Figure 1: Scheme showing the axes defined in the text for the CH_2 and CH_3 units.

References

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