

Parametrization scheme with accuracy and transferability for tight-binding electronic structure calculations with extended Hückel approximation and molecular dynamics simulations

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Received: 13 June 2012 / Accepted: 14 January 2013 / Published online: 12 February 2013
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Abstract A transferable tight-binding parametrization procedure for extended Hückel approximation is proposed, with the charge self-consistent scheme, that could be applied to the quantum molecular dynamics (MD) simulation for long-time dynamics of large-scale systems. In this procedure, either a target molecule is divided into small molecules or another realistic set of small molecules characterizing chemical bonds in the complicated target molecule is adopted. Then, the parameters for these small molecules are adjusted and compared with reference results of energy levels and wave functions by, for example, density functional theory. Upon application to the large target molecule, these parameters are then readjusted directly in the target molecule. An example is demonstrated with MD simulation applied to the ionic liquid molecule N-methyl-N-propylpiperidinium bis trifluoromethanesulfonyl imide (PP13-TFSI). The origin and stability of HOMO–LUMO gap are discussed.

Keywords Extended Hückel approximation · Charge self consistent scheme · Tight-binding molecular dynamics simulation · Ionic liquid PP13-TFSI

Introduction

The tight-binding (TB) method continues to play an important role in quantum chemistry and physics, mainly due to

its high capacity to give qualitative insight into chemical bonding, even though nowadays ab initio electronic structure calculation methods based on the density functional theory (DFT) are widely used. Moreover, combining quantum molecular dynamics (MD) with the TB method (TB-MD scheme) is useful and powerful, particularly for simulating long-term dynamic processes from several hundreds of picoseconds to nanoseconds in large size systems of several tens of thousands of atoms, so that the TB-MD scheme has been applied to a wide range of materials and phenomena.

Many studies have reported improved accuracy and transferability of the extended Hückel approximation (EHA) [1–6]. TB methods with the charge self-consistent (CSC) scheme can treat more qualitatively materials in which electron charges transfer appreciably among ions [7]. Optimized parameter sets for the semi-empirical molecular orbital (MO) method, such as the modified neglect of diatomic overlap (MNDO) method [8, 9], have accumulated and calculations succeed in well describing the heat of formation and other physical and chemical properties of many molecules. Furthermore, improvement of the Slater-type orbitals (STO) was proposed recently and it was found that the double- ζ STOs for s- and p-orbitals can reproduce accurately the electronic band structures of crystalline solids by the TB scheme with EHA [10].

However, it is recognized that the parameters of EHA must be determined empirically, and no efficient parametrization scheme has yet been established. It is very difficult to determine a parameter set because it depends sensitively on the local system environment. In fact, even though well optimized parameter sets might possibly give accurate results for tested molecules, they might not guarantee applicability to other molecules or compounds, especially complicated molecules, i.e., there is a lack of transferability. In addition, we have often faced the difficulty of having no

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optimized parameters for target molecules, so that few TB studies with EHA have been achieved for unconventional molecules and novel materials. The essential cause of this difficulty may be the absence of a transferable parametrization scheme with clear physical or chemical meanings of parameter adjustment procedure for target molecules and materials, even though a general procedure of atom-superposition and electron-delocalization (ASED) band theory has been established [11]. After several attempts at EHA, we found that ζ parameters for the extent of STO do not depend sensitively on a compound itself, once the valency of ions is fixed, and that, on the contrary, the environment has a great effect on the relative difference of atomic energy.

Stimulated by wanting to solve these fundamental problems, we have attempted to construct a transferable parametrization scheme in the TB formalism with EHA, so as to contribute to wider application of the TB-MD calculation. In this paper, details of the parametrization procedure of EHA are presented for, as an example, a molecule of N-methyl-N-propylpiperidinium bis trifluoromethanesulfonyl imide (PP13-TFSI), which is one of ionic liquids attracting much attention because of its unconventional solvent properties. Ionic liquid PP13-TFSI is a prospective candidates for an electrolyte in lithium secondary batteries due to its valuable properties such as low flammability, negligible vapor pressure, and chemical stability. Hence, PP13-TFSI has been the subject of many studies, both experimental and theoretical [12–15]. However, it is widely known that the slow dynamics of ionic liquids requires long simulations during which DFT cannot determine the dynamic properties of materials [16–19]. In addition, charge transfer is expected to play an important role in the formation of a solvation shell in ionic liquid solvents. However, classical MD simulation treats charge transfer effects as a change in electrostatic potential and a small deviation of interaction parameters (e.g., spring constants between atoms). It is barely possible for classical MD simulations to include a change of bonding character. As such, simulation studies on ionic liquids remain challenging. The following section “Extended Hückel approximation and charge self consistency” gives a brief review of EHA, and explains CSC theory. In “Determination of TB-parameters of extended Hückel approximation”, we explain details of the parameter optimization procedure using the example of a H₂O molecule. The section entitled “Molecular dynamics simulation of PP13-TFSI molecule” is devoted to a preliminary TB-MD simulation of PP13-TFSI, and the results of the simulation confirm the effectiveness of our parametrization scheme with EHA. The final section (“Molecular dynamics simulation of PP13-TFSI molecule”) summarizes the present work.

Extended Hückel approximation and charge self consistency

The total molecular charge density is given as

$$\rho(\mathbf{r}, \mathbf{R}_{a_1}, \mathbf{R}_{a_2}, \dots) = \sum_{a_i} \rho_{a_i}(\mathbf{r} - \mathbf{R}_{a_i}) + \rho_{npf}(\mathbf{r}, \mathbf{R}_{a_1}, \mathbf{R}_{a_2}, \dots), \quad (1)$$

where \mathbf{R}_{a_i} represents the atomic position of an atom a_i , and $\rho_{a_i}(\mathbf{r} - \mathbf{R}_{a_i})$ and $\rho_{npf}(\mathbf{r}, \mathbf{R}_{a_1}, \mathbf{R}_{a_2}, \dots)$ are the spherical atomic charge of an atom a_i and the non-perfectly-following remainder [11]. Evaluation of the energy due to the electronic charge rearrangement requires knowledge of $\rho_{npf}(\mathbf{r}, \mathbf{R}_{a_1}, \mathbf{R}_{a_2}, \dots)$ which is not available. However, the extended Hückel-like delocalization energy generally provides a good approximation [11, 20]. The resultant total energy consists of the band energy and the repulsive energy, which are expressed, respectively, as

$$E_{tot} = \sum_i^{occ} \varepsilon_i + \sum_{a,b} E_{rep}(|\mathbf{R}_a - \mathbf{R}_b|), \quad (2)$$

$$E_{rep}(|\mathbf{R}_a - \mathbf{R}_b|) = \frac{Z_a Z_b}{R_{ab}} - \frac{Z_a}{2} \int d^3 \mathbf{r} \frac{\rho_b(\mathbf{r} - \mathbf{R}_b)}{|\mathbf{R}_{ab} - \mathbf{r}|} - \frac{Z_b}{2} \int d^3 \mathbf{r} \frac{\rho_a(\mathbf{r} - \mathbf{R}_a)}{|\mathbf{R}_{ab} - \mathbf{r}|}. \quad (3)$$

Here, ε_i is the MO energy of the level i , $\mathbf{R}_{ab} = \mathbf{R}_a - \mathbf{R}_b$, Z_a is an effective core charge, and $\rho_a(\mathbf{r})$ is the electron density of the atom a .

The MO ψ_α can be obtained by solving a generalized eigenvalue equation;

$$H\psi_\alpha = \varepsilon_\alpha S\psi_\alpha, \quad (4)$$

$$\psi_\alpha = \sum_{a,nlm} C_{a,nlm}^\alpha \phi_{nlm}^{(a)}, \quad (5)$$

where H and S represent the Hamiltonian and the overlap matrices evaluated from MOs, respectively, and MOs are expressed by a linear combination of atomic orbitals $\phi_{nlm}^{(a)}$ of the principal, angular and magnetic quantum numbers (n, l, m).

We introduce a further approximation into atomic orbitals, i.e., we adopt STOs $\phi_{nlm}^{STO(a)}(\mathbf{r} - \mathbf{R}_a)$ of an atom a represented with an STO parameter ζ_l as

$$\phi_{nlm}^{STO(a)}(\mathbf{r}) = R_{nl}^{(a)}(r) Y_l^m(\theta, \phi), \quad (6)$$

$$R_{nl}^{(a)}(r) = \sqrt{\frac{(2\zeta_l^a)^{2n+1}}{(2n)!}} r^{n-1} \exp(-\zeta_l^a r), \quad (7)$$

where Y_l^m is the spherical harmonics. The matrix elements of the overlap matrix can be calculated from the STOs. The diagonal elements H_{ii} of the Hamiltonian H are empirically determined from ionic energies and the off-diagonal elements of H are determined in EHA as follows;

$$H_{ii}^0 = \varepsilon_i^{atom} \tag{8}$$

$$H_{ij}^0 = K(R_{ij}) \frac{H_{ii} + H_{jj}}{2} S_{ij} \quad (i \neq j), \tag{9}$$

where ε_i^{atom} is the atomic energy. The modified Wolfsberg-Helmholtz constant K represents the distortion of wavefunctions and is a function of an inter-atomic distance R_{ij} described as [5]

$$K(R) = 1 + (\kappa + \Delta^2 - \Delta^4 \kappa) \exp[-\delta(R - d_0)/q], \tag{10}$$

$$\Delta = \frac{H_{ii} - H_{jj}}{H_{ii} + H_{jj}}, \tag{11}$$

$$q = 1 + [(R - d_0) - |R - d_0|]^2 \delta^2. \tag{12}$$

The parameter δ is a damping factor for inter-atomic distances further than $d_0 = n^A/\zeta^A + n^B/\zeta^B$, and the parameter κ enhances interactions between orbitals. In the present study, we fix them at the standard values of $\delta = 0.13 \text{ \AA}^{-1}$ and $\kappa = 0.75$.

The repulsive interaction E_{rep} is sometimes too large at long distances so that inter-atomic distance and MO energy levels could not be determined consistently. Then, we introduce a parameter ζ^* in the charge density $\rho_a(\mathbf{r})$ only in the repulsive energy E_{rep} part (3) as $\zeta' = \zeta^* \cdot \zeta$ and refer to this as $E_{rep}(\zeta^*)$.

A serious problem in the conventional TB-scheme is the treatment of fixing the Hamiltonian independent of electron charge transfer. The CSC calculation proposed by Elstner et al. [7] is adopted in the present scheme in order to handle the charge transfer effect correctly. The Mulliken fluctuation charge is calculated at each iteration step. The resultant Mulliken charges can reproduce quantitatively those of the DFT calculations and will be compared with DFT results in a later section.

If the resultant charge density $\rho(\mathbf{r})$ is not equal to the starting charge density $\rho^0(\mathbf{r})$, which is almost always the case, we have the energy deviation (the second order energy) [7]

$$E_{2nd} = \frac{1}{2} \sum_{a,b} \int d^3\mathbf{r} \int d^3\mathbf{r}' \Gamma[\mathbf{r}, \mathbf{r}' : \rho^0] \delta\rho_a(\mathbf{r}) \delta\rho_b(\mathbf{r}'). \tag{13}$$

Equation (13) can be expressed as

$$E_{2nd} = \frac{1}{2} \sum_{a,b} \Delta q_a \Delta q_b \gamma_{ab}, \tag{14}$$

where the charge fluctuation is approximated as

$$\delta\rho_a(\mathbf{r}) \simeq \Delta q_a F_{00}^a(|\mathbf{r} - \mathbf{R}_a|) Y_{00}(\mathbf{r} - \mathbf{R}), \tag{15}$$

and Δq_a is the deviation of the resultant Mulliken charge from the starting one.

Then, the total energy and the Hamiltonian are modified as [7]

$$E_{tot} = \sum_i^{occ} \varepsilon_i + \sum_{a,b} E_{rep}(\zeta^*) + E_{2nd}. \tag{16}$$

The parameter γ_{ab} introduced in Eq. (14) is defined as [7]

$$\gamma_{ab} = \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho_a(\mathbf{r}) \rho_b(\mathbf{r}')}{|\mathbf{R}_{ab} + \mathbf{r} - \mathbf{r}'|}, \tag{17}$$

which is a function of the interatomic distance $|\mathbf{R}_{ab}|$ and the diagonal terms γ_{aa} and γ_{bb} . The quantity γ_{aa} is the chemical hardness or the Hubbard parameter, and could be evaluated by the difference between the ionization and the electron affinity energies. In our actual calculations, the highest occupied atomic level is used as the chemical hardness for each atom.

Consequently, the matrix element of the Hamiltonian is given as

$$H_{ij} = H_{ij}^0 + H_{ij}^{CSC}, \tag{18}$$

$$H_{ij}^{CSC} = \frac{1}{2} S_{ij} \sum_k (\gamma_{ik} + \gamma_{jk}) \Delta q_k. \tag{19}$$

In the present formalism of the modification of the EHA, we chose parameters adjusted to the atomic levels $\varepsilon_i^{atom} = H_{ii}$, the STO parameters ζ , and the degree of screening effect (rescaling) for the repulsive part ζ^* . Hereafter, we refer to these parameters as TB-parameters of extended Hückel approximation (TB-EHA parameters). It should be noted that, in the present study, we used single- ζ STOs.

Determination of TB-parameters of EHA

Determination procedure for TB-EHA parameters

The procedure of our parametrization scheme (for TB-EHA parameters) is represented schematically in Fig. 1. It should be stressed that careful consideration of electronic states was used to clarify the physical meaning of the parameter adjustment procedure.

The procedure of determining TB-EHA parameters consists of three steps for a given complicated molecule as follows:

- (1) separation of small molecules consisting of the target molecule or choice of small real molecules characterizing chemical bonds in the target complicated molecule,
- (2) parameter adjustments for small molecules, and
- (3) “readjustment” of these parameters by applying those adjusted parameters directly to the target molecule.

In the procedure (2), physical quantities such as bond length and bond angle dependence of the total energy, energy levels, and wavefunctions of eigen states are calculated both by EHA and DFT methods (or other reference method) and the behavior of MO levels and the character of eigen states are observed. In procedure (3), one calculates the electronic structure of the target molecule by using the adjusted parameter set, and compare the density of states (DOS) and the typical character of some eigen states with those obtained by reference DFT calculations. The “readjustment” of parameters is thus necessary in order to calculate accurate electronic structures and to perform TB-MD of large systems.

We demonstrate our parametrization scheme by treating an ionic liquid molecule PP13-TFSI consisting of H, C, N, O, S, and F atoms (Fig. 2). All calculations based on the EHA are achieved by the extra-large scale electronic structure (ELSESES) calculation package [21]. Other application studies with ELSESES may be found in the literature [22–24]. A reference DFT calculation with B3LYP hybrid functional and STO-3G basis set was performed using the Gaussian 09 package [25].

Parameter adjustments using small molecules: the example of H₂O

First, we chose small molecules, H₂O, CO₂, NO₂, SO₂ and CF₄, of constituent atoms or ions of PP13-TFSI [procedure (1)]. For example, though a N–O bond does not appear in PP13-TFSI, the geometry of NO₂ or the N–O bond may be similar to that of a fictitious molecule NS₂ or a N–S bond in PP13-TFSI. The resultant adjusted parameters for these molecules are expected to reproduce faithfully the chemical bonds in PP13-TFSI. Following procedure (2), parameter adjustment was carried out on small molecules. Here, we first fixed those parameters of H, then adjusted those of O, and then those of C, and so on (H → O → C, N, S → F). We show details of the parametrization scheme of the H₂O molecule as an example in the following. All TB-EHA parameters of H atom are fixed at $\varepsilon_{1s}^H = -13.6$ eV and $\zeta_{1s}^H = 1.3$ (1/au).

Since the creation of a dipole moment is crucial in the geometry of the H₂O dimer, one possible method for MD simulation of water would be to include 2p orbitals in the H atom. It should be noted that a sophisticated dipole interaction term was introduced recently, and the TB Hamiltonian successfully treats the MD of liquid water [26].

STO parameters in the EHA

Parameter adjustment is achieved systematically in accordance with the hierarchical structure of cohesive energy, i.e., (difference between) atomic energies, two-center energies (determining bond lengths), three-center energies (determining bond angles) and delocalization energies (due to extended charge).

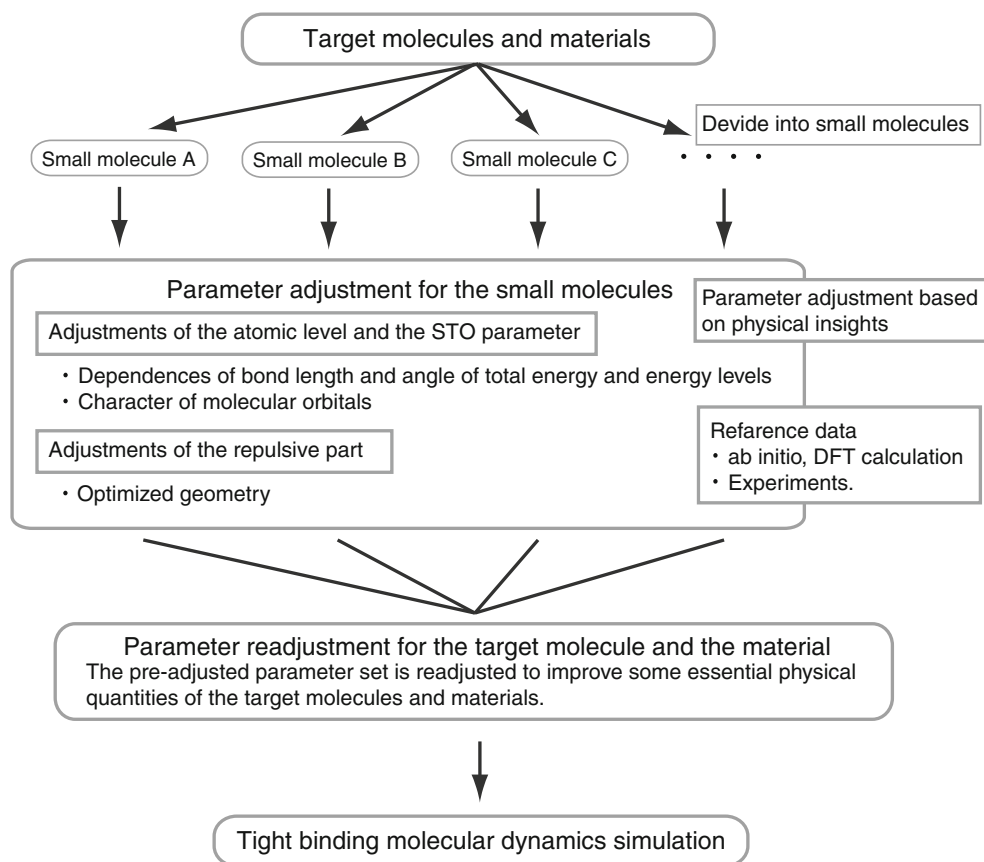
We first calculated bond length and bond angle dependence of the total energy with a starting parameter set of $\varepsilon_{2s}^O = -28.2$ eV, $\varepsilon_{2p}^O = -12.4$ eV, $\zeta_{2s}^O = 2.575$ (1/au), $\zeta_{2p}^O = 2.275$ (1/au), and $\zeta^* = 1.0$, compared with DFT calculation with B3LYP hybrid functional and STO-3G basis. Figure 3 shows the bond length dependence of the total energy with the starting parameter set. The resultant equilibrium O–H bond length is 1.123 Å and the equilibrium bond angle 114.6° (cf. experimental values of 0.960 Å and 104.5°). The bond length dependence of the total energy does not show a clear stable minimum thus the parameters required to be adjusted.

Figure 4 shows bond length and bond angle dependence of MO energies calculated by using the starting parameter set for the O atom, compared with DFT calculation with B3LYP/STO-3G. The bond length dependence of the total energy could be adjusted by using the rescaling parameter ζ^* , and then the bond angle dependence may be first adjusted at this earlier stage. One may note from Fig. 4b that the starting TB-EHA parameter set does not reproduce the behavior of MO energies. The order of energies of MOs is an additional property, and the resultant order is (in the energy region above –30 eV from lower side near the equilibrium value of bond angle): 1A₁, 1B₂, 2A₁, 1B₁, 2B₂, 3A₁, ⋯. The DFT calculation with B3LYP/STO-3G predicts the order 1A₁, 1B₂, 2A₁, 1B₁, 3A₁, 2B₂, ⋯. Highest occupied MO (HOMO) level is 1B₁ and the order of occupied MO levels is identical.

The MO levels of 1B₂, 1B₁ and 1A₁ have their own individuality in their bond angle dependence; e.g., the MO energy of 1B₂ decreases, that of 1B₁ is almost constant and that of 2A₁ increases with increasing bond angle. Therefore, in order to decrease the equilibrium bond angle, one should find parameters that change either the MO energy of 1B₂ or that of 2A₁ more slowly with changing bond angle.

Atomic energies are set initially to be those of isolated atoms evaluated by the DFT calculation. At this stage, it is

Fig. 1 The flow of the adjustment procedure of tight binding-parameters of extended Hückel approximation (TB-EHA parameters)



essentially important not to change the intervals of atomic energies between different atoms and different orbitals. Each isolated MO level can be estimated mainly from the atomic levels especially in a long bond length region. The atomic energy is then adjusted on the basis of physical

consideration to fit the bond angle or bond length dependence of the MO energies.

Wave functions of these MO levels are depicted in Fig. 5. We can see their bonding or anti-bonding character and plan a strategy for choosing appropriate values of parameters. In the present example of H₂O: (2-i) since 1B₁ is a non-

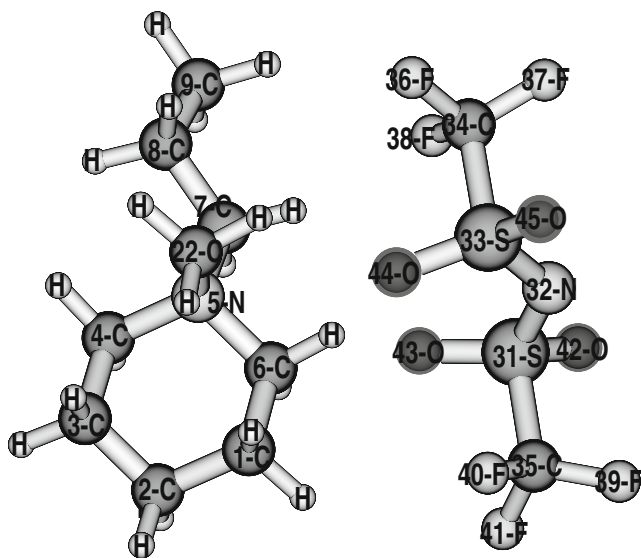


Fig. 2 Molecular structure of N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI). Element symbols and numbering of atoms are depicted on the atomic spheres

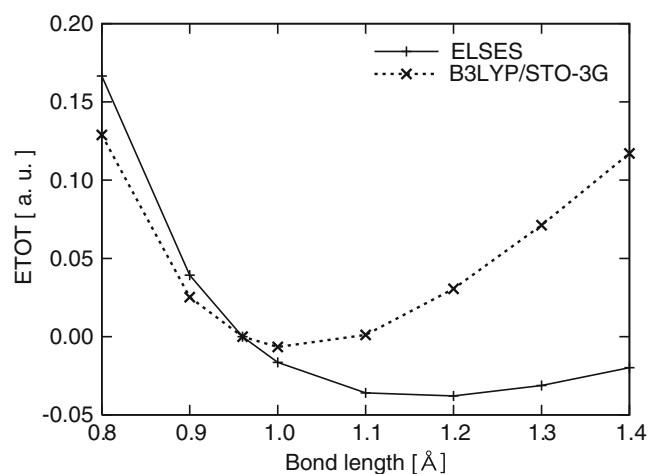


Fig. 3 Bond length dependence of the total energy of the H₂O molecule with a starting Slater-type orbitals (STO) parameter set (see text), compared with the density functional theory (DFT) calculation with B3LYP/STO-3G. The energy zero point coincides with the total energy at the equilibrium geometry of the DFT results

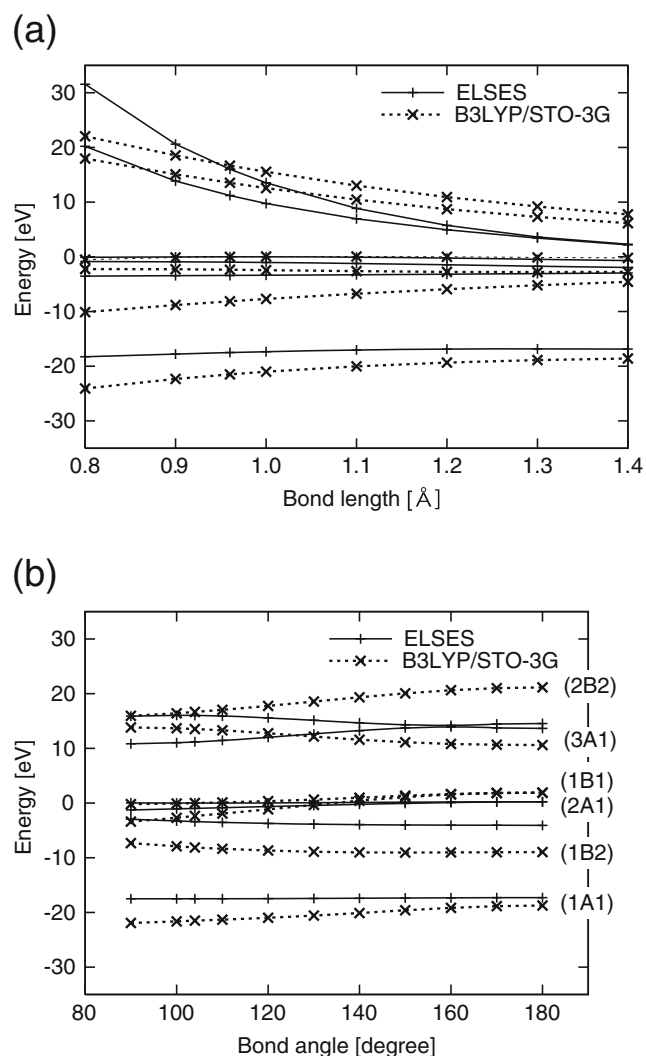


Fig. 4 **a** Bond length dependence, and **b** bond angle dependence of molecular orbital (MO) levels of a H₂O molecule with the starting TB-EHA parameter set for an O atom, compared with DFT calculation with B3LYP/STO-3G. The energy zero point is at the top of the occupied MO energy at the equilibrium geometry of bond length and bond angle determined experimentally

bonding orbital of O-2p_z, one can find a value of ε_{2p}^O by adjusting its MO energy. (2-ii) MO energy of 1A₁ level is determined by ε_{2s}^O and ζ_{2s}^O and one can find these values by adjusting the 1A₁ MO energy. The MO energies of 2A₁ and 3A₁ levels (contributed by oxygen 2p_x) depend not only on ε_{2s}^O and ζ_{2s}^O but also on ε_{2p}^O and ζ_{2p}^O . (2-iii) Because MO energies of the B₂-group (contributed by oxygen 2p_x or 2p_y orbitals) are determined mainly by ζ_{2p}^O , one can find a value of ζ_{2p}^O by adjusting their MO energy intervals. Thus, (2-ii) and (2-iii) are explained in more detail as follows:

The change of ε_{2s}^O affects only the levels of A₁ states, as described in (2-ii) above. After testing several values, we

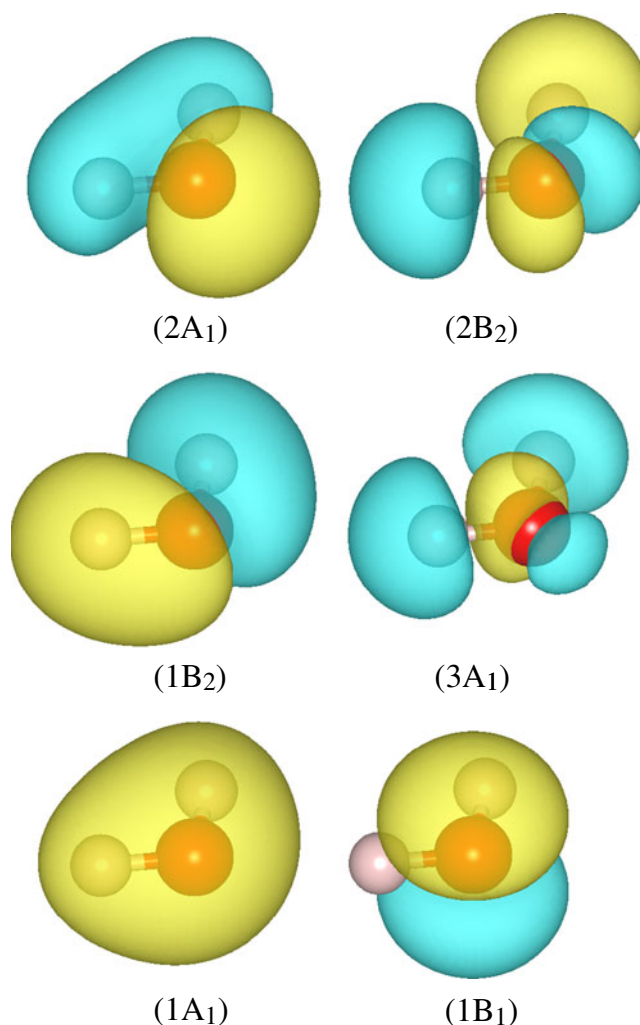


Fig. 5 Eigen states of the H₂O molecule. The colors yellow and blue show the phases of wave functions

chose $\varepsilon_{2s}^O = -33.2$ eV with an agreement of 1A₁ MO energy and better agreement of excited states 3A₁ and 2B₂. Now the energy order of MO levels agree with the DFT calculation.

Next, we adjust STO parameters ζ by considering the bonding or anti-bonding nature between atomic orbitals. In the case of the H₂O molecule, since energy levels of occupied MO states depend weakly on the bond angle, the change of ζ_{2s}^O seems not to affect the behavior of energy levels. However, in fact, the energies of the occupied A₁ states are slightly shifted. From these trials, we chose the STO parameter $\zeta_{2s}^O = 3.175$ (1/au) to fit the DFT calculation.

The same procedure was executed for the STO parameter ζ_{2p}^O , and all TB-EHA parameters of the oxygen atom were then fixed. Figure 6 shows the bond length and bond angle dependence of MO levels after readjusting all TB-EHA parameters.

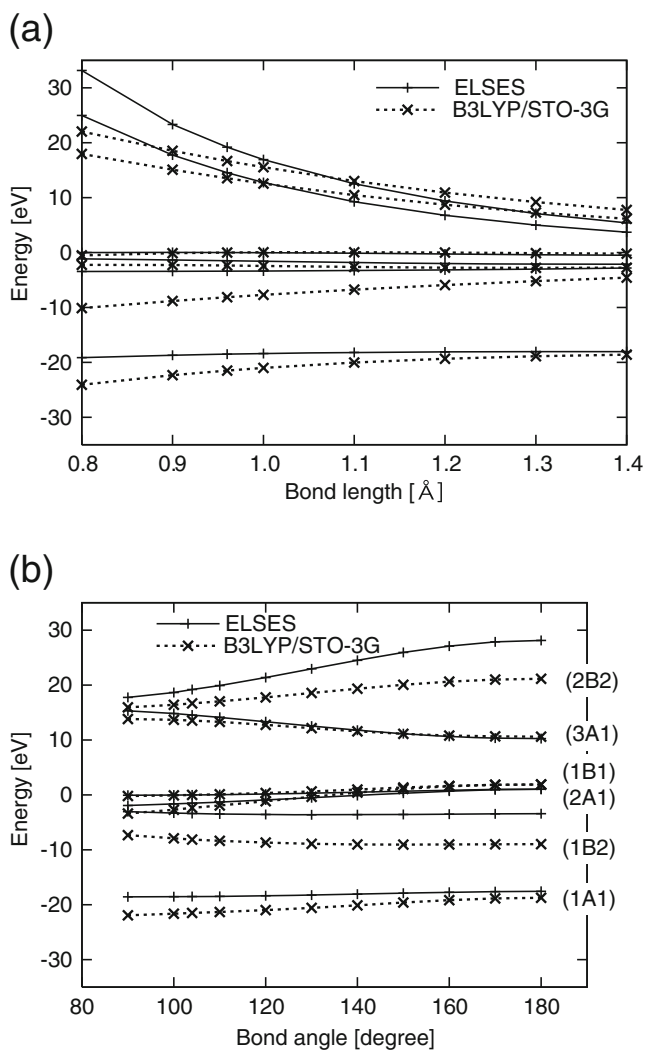


Fig. 6a, b Dependence of energy levels for the H₂O molecule, compared with DFT calculation by B3LYP/STO-3G method, with the final adjusted parameters for O atoms of $\epsilon_{2s}^O = -33.200$ eV, $\epsilon_{2p}^O = -15.877$ eV, $\zeta_{2s}^O = 3.175$ (1/au), and $\zeta_{2p}^O = 1.950$ (1/au). **a** Bond length dependence, and **b** bond angle dependence. The energy zero point is the same as in Fig. 4

Repulsive rescaling parameters

MO energies are independent of the repulsive rescaling parameter ζ^* . Of course, ζ^* changes E_{rep} in the total energy and, therefore, changes the equilibrium bond lengths and bond angles. Therefore, after fixing all other TB-EHA parameters, ζ^* should be adjusted to obtain the accurate molecular geometry.

After optimization of STO parameters without repulsive rescaling ($\zeta^* = 1.0$), the O–H bond length R_{OH} was found to be 1.464 Å and the H–O–H bond angle 93.07°. These results overestimate the repulsive energy between O and H atoms. Then, in order to weaken the repulsive Coulomb interaction between O and H, we chose a value of $\zeta^{*O} = 1.6$.

The total energies before and after the repulsive rescaling procedure are compared in Fig. 7, together with that of DFT calculation. After this adjustment, the O–H bond length was found to be 1.074 Å and the H–O–H bond angle 102.9°, which are much closer to the experimental values of 0.96 Å and 104.5°, respectively. The results may be fairly good, though the cohesive energy is not deep enough, compared with that of the DFT calculation.

The resultant Mulliken charges of an H₂O molecule in the EHA are –0.520 (in O) and 0.260 (in H), compared with the DFT results –0.366 (in O) and 0.183 (in H). Thus, agreement is fairly good.

Summary of parameters for PP13-TFSI from results of small molecules

The above procedure explained for H₂O was applied to other isolated molecules CO₂, NO₂, SO₂ and CF₄, for which we followed the procedure in that order. Then, when attempting to determine TB-EHA parameters of N in NO₂, we use those of O determined in H₂O. All TB-EHA and repulsive rescaling parameters were optimized as shown in Table 1.

The DOS of the PP13-TFSI molecule is shown in Fig. 8 (“pre-adjusted”), together with that of the DFT calculation. The atomic configuration here was optimized using the ELSES package tool and is very similar to that optimized by the DFT calculation with B3LYP/STO-3G [24]. We can see that the essential feature of DOS with optimized TB-EHA parameters (in Table 1) corresponds well to those obtained using the DFT calculation.

The wavefunctions of HOMO and the lowest unoccupied MO (LUMO) of PP13-TFSI are depicted in Fig. 9, and the

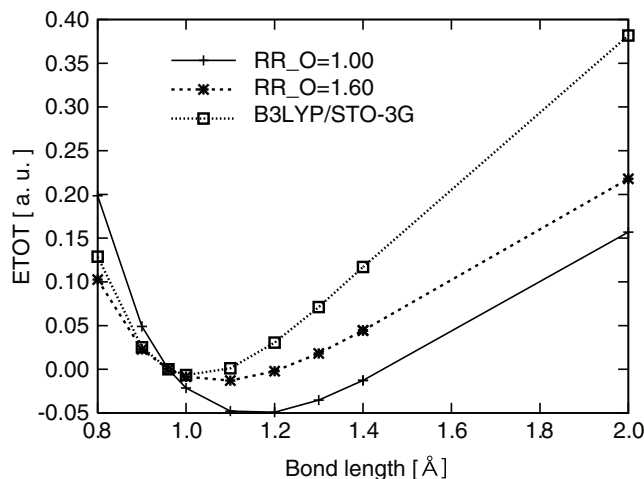


Fig. 7 Total energy of H₂O molecule before and after the repulsive rescaling of ζ^* for an oxygen atom. Other TB-EHA parameters of the oxygen atom are fixed as $\epsilon_{2s}^O = -33.20$ eV, $\epsilon_{2p}^O = -15.877$ eV, $\zeta_{2s}^O = 3.175$ (1/au) and $\zeta_{2p}^O = 1.950$ (1/au)

Table 1 Optimized tight binding-parameters of extended Hückel approximation (TB-EHA) parameters for small molecules H₂O, NO₂, SO₂ and CF₄ and the “readjusted” ζ and repulsive rescaling parameter ζ^* for N-methyl-N-propylpiperidinium bis trifluoromethanesulfonyl imide (PP13-TFSI) molecules

Element	AO	Atomic level [eV]	ζ (1/au)	“Readjusted” ζ (1/au)	ζ^*	“Readjusted” ζ^*
H	1s	-13.600	1.300	1.300	1.0	1.0
	2s	-25.840	2.400	2.400	1.0	1.3
C	2p	-15.870	1.525	1.525	1.0	1.3
	2s	-28.300	1.700	1.700	1.3	1.3
N	2p	-16.337	1.600	1.600	1.3	1.3
	2s	-33.200	3.175	3.175	1.6	1.6
O	2p	-15.877	1.950	1.950	1.6	1.6
	2s	-37.860	3.510	3.510	2.0	2.0
F	2p	-16.060	2.225	2.225	2.0	2.0
	3s	-23.500	2.000	2.000	1.1	1.1
S	3p	-11.800	1.900	1.750	1.1	1.1

character of these eigen states is identical to that determined by DFT calculation. However, several differences were found in level-spacings and the HOMO–LUMO gaps do not agree with each other. Hereafter, we refer to the parameter set at this stage as the ‘pre-adjusted’ parameter set.

“Readjustment” of parameter set for the target molecule PP13-TFSI

Now, we show the final step, the “readjustment” procedure of the parameter set, to perform accurate electronic state calculations (and MD simulations) of a target molecule. This readjustment is necessary due to the difference in electrostatic environment between small isolated molecules and the larger target molecule. We readjust the parameter set to fit only essential physical quantities (e.g., the MO energies or the DOS), because complete readjustment of many physical quantities is not feasible.

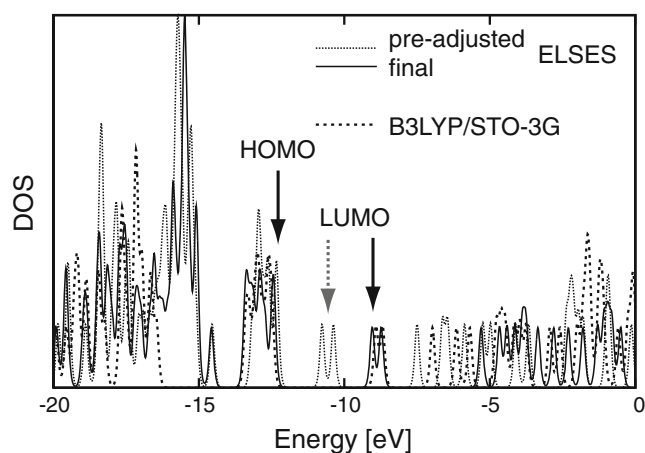


Fig. 8 Density of states (DOS) of PP13-TFSI with parameters before readjustment (‘pre-adjusted’) and that with readjusted parameters (‘final’). The HOMO–LUMO gap is smaller in the former case, compared with that of DFT calculation, and improved by the readjustment procedure

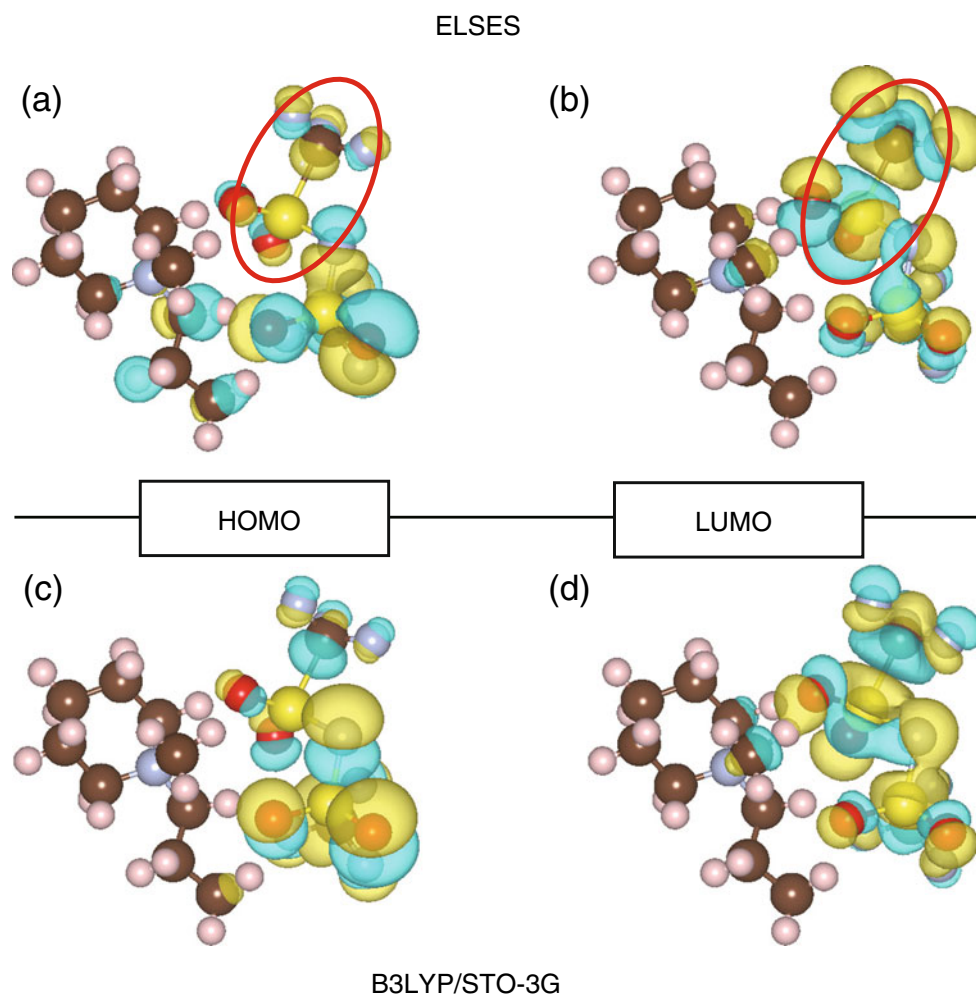
We noted already that several level spacings and the HOMO–LUMO gap show a discrepancy with the reference DFT results. The HOMO–LUMO gap may be seriously important when we deal with mixture solvent of PP13-TFSI molecules and other ions or molecules, since we expect a large amount of charge transfer. Here, we show how to improve the HOMO–LUMO gap quantitatively as an example of parameter readjustment for the target molecule without changing the values of many parameters.

The HOMO–LUMO gap obtained by calculation with the pre-adjusted TB-EHA parameters is 1.55 eV, i.e., smaller than the 3.4 eV obtained by DFT calculation. In order to improve agreement of the HOMO–LUMO gap, we carefully analyzed the character of HOMO and LUMO. It was observed that no amplitude of HOMO wavefunction exists on the S atom, and anti-bonding character in LUMO is seen between the S atom and the C atom, as indicated by the red circle in Fig. 9. This implies that the energy level of HOMO does not depend on the TB-EHA parameters of S atoms, and that, with decreasing magnitude of ζ_{3p}^S , the anti-bonding character of LUMO increases. As a result, with decreasing ζ_{3p}^S , the energy level of LUMO shifts and the HOMO–LUMO gap would open wider. On the basis of this physical insight, we readjusted the TB-EHA parameters of S atom as $\zeta_{3p}^S = 1.750$ (1/au), so that the DOS and HOMO–LUMO gap were improved as shown also in Fig. 8.

Final optimized “readjusted” ζ and ζ^* are listed in Table 1. It should be noted that the repulsive rescaling parameter of C-atom is changed slightly and reproduces an accurate stable structure.

A good test would be to compare the resultant bond lengths in N–C (1.73 Å in average), N–S (1.72 Å), and C–S (2.24 Å) with the DFT results N–C (1.57 Å on average), N–S (1.89 Å), and C–S (2.25 Å). This results show a fair agreement with those of the reference system and support our adoption of the NO₂ molecule instead of a fictitious NS₂.

Fig. 9 HOMO (a, c) and LUMO (b, d) of PP13-TFSI, by the present method (calculated using the ELSES package) and DFT calculation (B3LYP/STO-3G)



We also check the effect of the final adjustment on SO_2 and CF_4 molecules. The readjustment of the TB-EHA parameters of the S atom does not affect the behavior of the SO_2 molecule except a slight elongation of the S-O bond length 1.83 Å (from 1.75 Å) that can be compared to a value 1.6 Å of DFT calculation. The readjustment of the parameters of the C atom causes shortening of the C-F bond length to 1.473 Å (from 1.575 Å), which is comparable to the value 1.421 Å of the DFT calculation.

The resultant Mulliken charge in a stable configuration is also summarized in Table 2, confirming the overall agreement of the results with those obtained by DFT calculation with B3LYP/STO-3G.

Molecular dynamics simulation of PP13-TFSI molecule

We performed a TB-MD simulation of the PP13-TFSI molecule, using the ELSES package, for a time period of 100 ps

Table 2 Mulliken charge of PP13-TFSI. The numbers of atoms correspond to those in Fig. 2. The column 'DFT' indicates the results by DFT calculation with B3LYP/STO-3G

Element	ELSES	DFT	Element	ELSES	DFT	Element	ELSES	DFT
1-C	-0.27	-0.15	2-C	-0.29	-0.14	3-C	-0.28	-0.15
4-C	-0.31	-0.06	5-N	-0.37	-0.12	6-C	-0.36	-0.06
7-C	-0.36	-0.06	8-C	-0.26	-0.14	9-C	-0.48	-0.23
22-C	-0.52	-0.17	31-S	1.32	1.18	32-N	-0.68	-0.78
33-S	1.34	1.18	34-C	-0.08	0.20	35-C	-0.06	0.20
36-F	-0.04	-0.12	37-F	-0.03	-0.11	38-F	-0.03	-0.14
39-F	-0.01	-0.13	40-F	-0.03	-0.12	41-F	-0.03	-0.11
42-O	-0.61	-0.54	43-O	-0.63	-0.56	44-O	-0.64	-0.56
45-O	-0.57	-0.53	H	0.13~0.25	0.08~0.16			

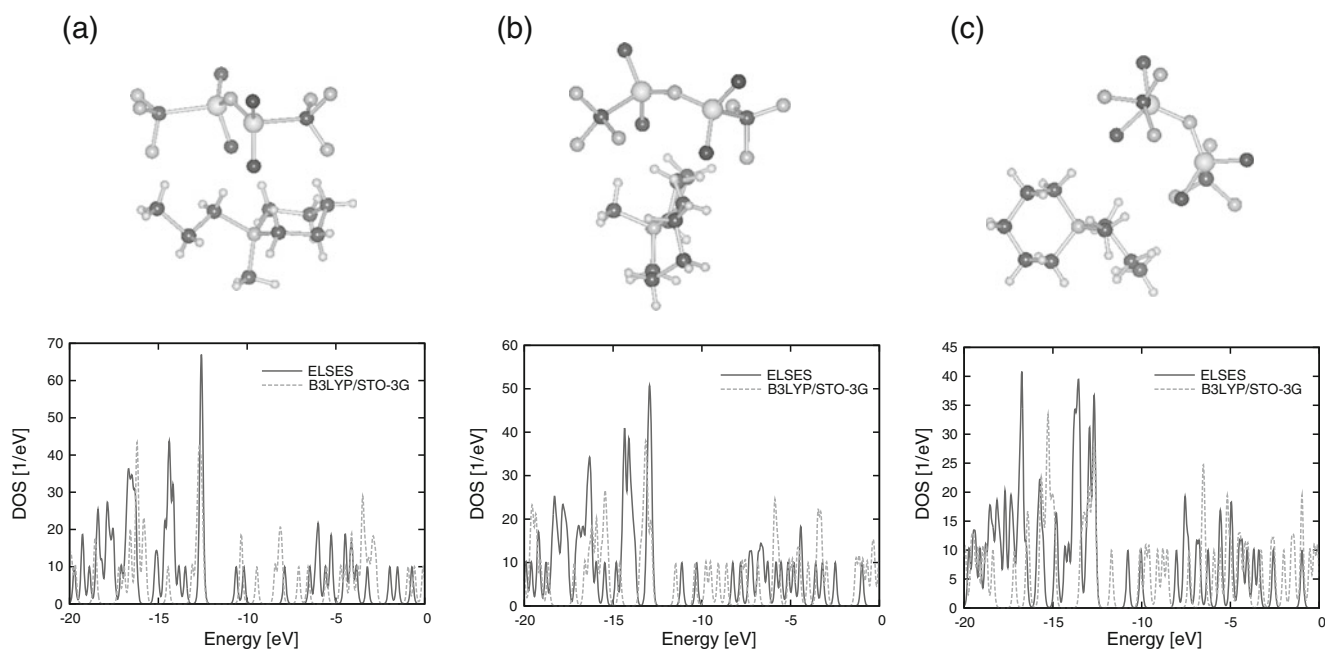


Fig. 10a–c Quantum molecular dynamics simulations of the PP13-TFSI molecule. The HOMO–LUMO gap is always located between -10 eV and -8 eV. *Top* Snapshots of the molecules. *Bottom*: DOS (solid lines), compared with those obtained by DFT (dotted lines). The

DOS by DFT theory was calculated using the same molecular configuration as that obtained with TB-MD simulation. Snapshots are at time $t=25$ ps (a), 50 ps (b), and 75 ps (c)

under a free boundary condition, in order to clarify the validity of the resultant optimized parameters, molecular motions, and behavior of electronic state throughout the simulation. In the simulation, the temperature was controlled by the Nose-Hoover thermostat and was set to 303 K.

Figure 10 shows some snapshots of the PP13-TFSI molecule and the corresponding DOS in the MD simulation, together with DOS of LDA, but in the same molecular configuration. The HOMO–LUMO gap survives through the MD simulations with large fluctuation, although the configuration of the cation (PP13) and the anion (TFSI) changes, and depends strongly on the interaction between S and C atoms on the anion as mentioned above. The thermal fluctuation of the distance between S and C atoms on the anion results in fluctuation of the HOMO-LUMO gap. The gap in Fig. 10c becomes very narrow in DFT, because a certain unoccupied level on the PP13 cation at a higher energy shifts downwards below the original LUMO level, in contrast to the present ELSES calculation. This might not happen if we could achieve the MD-simulation with DFT calculation, because the DFT calculation does not allow too long C–N and C–C distances in the PP13 cation but these sometimes happen in the present TB-MD calculation. This is one of problems with the repulsive interaction that we have not solved yet.

We found that the ion pair of a cation and an anion is quite stable in a PP13-TFSI molecule and no spontaneous dissociation was observed under the simulation conditions.

This dynamic behavior is also confirmed by the radial distribution function between N atoms on a cation and an anion, with a single peak of width 0.7 Å at around 6 Å and no intensity over 7 Å. This dynamic property was also observed in a subsequent study where TB-MD simulations of four PP13-TFSI ion pairs were performed using the optimized TB-EHA parameters [24]. The diffusion constant obtained by the study ($D=3.3 \times 10^{-11}$ m²/s) agrees fairly well with experimental observations [27].

Furthermore, we also performed an MD simulation of the solvent mixture LiTFSI+(PP13-TFSI)₃ for 100 ps with the same TB-EHA parameters [28]. The following was observed: (1) solvation formation as Li(TFSI)₂ and no diffusion of an isolated Li ion; and (2) diffusion of metal ions dressing the solvation shell becomes much slower. The results of this additional study reveal the validity of the TB-EHA parameter set. Details of the results of the TB-MD simulation of LiTFSI + (PP13-TFSI)₃ will be published elsewhere.

Conclusions

We have proposed a transferable TB parametrization scheme with the extended Hückel approximation which is independent of modeling, and have demonstrated the actual procedure in the ionic liquid molecule PP13-TFSI.

In the scheme, we first consider small molecules consisting of the target molecule or characterizing chemical bonds

in the target molecule. The parameter adjustment is carried out by comparing the bond angle and bond length dependence of MO energies, calculated by the Hückel approximation with the CSC scheme, with reference data (experimental values or data from DFT calculations). We determine atomic orbital energies from the levels of isolated atoms, and choose values of STO parameters by considering the bonding or antibonding characteristics between a certain atom-pair. We demonstrate the actual procedure of the determining parameter set of a H₂O molecule, in comparison with that obtained by DFT calculation. As such, the physical meaning of the parameter adjustment in our parametrization scheme is quite clear. At the next step of the procedure, we readjust the TB-EHA parameters considering the target molecule directly. In this step, we focus only on important physical quantities, because a complete description of many physical quantities is not feasible. We demonstrate the readjustment procedure for the PP13-TFSI molecule and demonstrate a good quantitative description of the HOMO–LUMO gap.

The quantum MD simulation of the PP13-TFSI molecule was demonstrated in order to test the validity of the resultant parameter set. The parameter set stabilizes the dynamic behavior of PP13-TFSI; no spontaneous dissociation of PP13-TFSI into cation and anion was seen under the simulation conditions. Furthermore, the diffusion constant and solvation geometry can be described in a plausible manner. The width of the HOMO–LUMO gap shows strong fluctuation, due mainly to the thermal vibration of the bond length in the anion. The thermal fluctuation might be enhanced too much and we thus observe too large a fluctuation of the HOMO–LUMO gap, which remains an open problem.

We have established a procedure for optimizing the TB parameters with EHA and CSC theory. We now believe that the TB parametrization scheme with EHA and the CSC theory can be applied to investigate the long-time dynamic behavior of a wide range of molecules and materials, although, at the present stage, the procedure to determine the parameter set requires time-consuming and careful treatment, especially for complicated molecules. We also applied the double- ζ STOs of Cerda et al. [10] to several materials and confirmed better agreement with reference DFT calculations. We are now in the process of coding a program of parameter determination for automatic optimization of the TB-EHA parameter set.

Acknowledgments We thank Hisatsugu Yamasaki, Satoru Yamamoto, Susumu Yamamoto and Takeo Hoshi for valuable discussions. Takeo Fujiwara expresses grateful gratitude to the TOYOTA Motor Corporation for financial support. Numerical calculation was carried out partly using Research Center for Computational Science, Okazaki, Japan. The molecular structures are visualized with the help of VESTA [29] and MOLDEN [30].

References

1. Hoffman R (1963) *J Chem Phys* 39:1397
2. Hoffman R (1964) *J Chem Phys* 40:2474
3. Hoffman R (1964) *J Chem Phys* 40:2745
4. Hoffman R (1964) *J Chem Phys* 40:2480
5. Wolfsberg M, Helmholz L (1952) *J Chem Phys* 20:837
6. Calzafferi G, Rytz R (1996) *J Phys Chem* 100:11122
7. Elstner M, Porezag D, Jungnickel G, Elsner J, Haugk M, Frauenheim T, Suhai S, Seifert G (1998) *Phys Rev B* 58:7260
8. Dewar MJS, Thiel W (1977) *J Am Chem Soc* 99:4899
9. Stewart J (1989) *J Comp Chem* 10(209):220
10. Cerdá J, Soria F (2000) *Phys Rev B* 61:7965
11. Nath K, Anderson AB (1990) *Phys Rev B* 41:5652
12. Tokuda H, Hayamizu K, Ishii K, Susan MABH, Watanabe M (2004) *J Phys Chem B* 108:16593
13. Tokuda H, Hayamizu K, Ishii K, Susan MABH, Watanabe M (2005) *J Phys Chem B* 109:6103
14. Abbott AP (2004) *J Phys Chem* 5:1242
15. Seki S, Kobayashi T, Kobayashi Y, Takaei K, Miyashiro H, Hayamizu K, Tsuzuki S, Mitsugi T, Umabayashi Y (2010) *J Mol Liq* 152:9
16. Pópolo TGD, Voth GA (2004) *J Phys Chem B* 108:1744
17. Borodin O, Smith GD (2006) *J Phys Chem B* 110:11481
18. Borodin O (2009) *J Phys Chem B* 113:11463
19. Bhargava BL, Balasubramanian S (2007) *J Chem Phys* 127:114510
20. Anderson AB (1975) *J Chem Phys* 62:1187
21. ELSSES package is available at <http://www.elses.jp>
22. Hoshi T, Iguchi Y, Fujiwara T (2005) *Phys Rev B* 72:075323
23. Iguchi Y, Hoshi T, Fujiwara T (2007) *Phys Rev Lett* 99:125507
24. Nishino S, Fujiwara T, Yamasaki H, Yamamoto S, Hoshi T (2012) *Solid State Ionics* 225:22
25. Frisch MJ et al (2009) Gaussian 09 Revision B 01. Gaussian, Inc, Wallingford
26. Paxton AT, Kohanoff JJ (2010) *J Chem Phys* 134:044130
27. Nicotera I, Oliviero C, Henderson WA, Appetecchi GB, Passerini SJ (2005) *J Phys Chem B* 109:22814
28. S. Nishino, T. Fujiwara, H. Yamasaki, S. Yamamoto, S. Yamamoto, T. Hoshi (2011) The 62nd Annual Meeting of the International Society of Electrochemistry. Niigata, Japan
29. Momma K, Izumi F (2008) *J Appl Crystallogr* 41:653
30. Schaftenaar G, Noordik JH (2000) *J Comput Aided Mol Des* 14:123