Atomic dynamics in superionic conductors by *ab initio* molecular-dynamics simulations

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Abstract

*Ab initio* computer-simulation techniques to study the atomic dynamics in superionic conductors are described. It is demonstrated that the superionic behavior in two typical superionic conductors, CuI and Ag₂Se, is successfully reproduced by means of *ab initio* molecular-dynamics simulations. A remarkable feature exhibited in the calculated partial pair distribution functions is that the nearest-neighbor distance for cation-cation pair is almost the same as that for cation-anion pair in spite of the correlation between the same type of ions, which has never been observed in classical computer simulations. We detail...
the method of population analysis to investigate the chemical properties of the mobile cations accompanied with the diffusive motion. It is found that the anomalously short cation-cation distance comes from an attractive interaction due to the hybridization of the atomic orbitals. It is also shown from the displacement-correlation functions that the mobile cations exhibit a collective diffusive motion with their neighboring cations.

I. Introduction
Superionic conductors are materials in which mobile ions migrate between sites in the sublattice of immobile ions [1–4]. They are characterized by both the liquid-like disordered structure of the mobile ions and the crystalline structure of the immobile ions. Although the study of these materials has a long history, fundamental questions concerning the microscopic origin and the mechanism of superionic behavior have not been sufficiently clarified yet. This may be attributed to the fact that the correlation between the dynamic properties of the mobile ions and the electronic states in these materials has not been investigated from first principles so far.

The atomistic computer simulation is a powerful tool for investigating properties of condensed systems which have a disordered structure of atoms. In most theoretical studies on the superionic conductors, molecular-dynamics (MD) simulations have been used with empirical interionic potential models [5–22]. These models reproduce the temperature dependence of the diffusion coefficient of the mobile ions, which is found to be in good agreement with that observed experimentally [5, 14, 18]. Moreover, some of the models have successfully described the nonsuperionic-superionic phase transitions occurring with the structural changes of the immobile ions [7, 10–12, 15, 21]. However, within these empirical models, the investigation on the microscopic origin of the superionic behavior is limited, since the empirical potentials lack the ability to describe the change of chemical bonding accompanied with the diffusive motion of the mobile ions. To clarify the microscopic mechanism of the high ionic conduction, it is essential to consider the electronic state around the mobile ions as a function of time, as has been suggested previously by the bond fluctuation model [23–25].

Some attempts to describe the high ionic mobility in the superionic conductors from first principles have been reported. Sarnthein et al. [26] have investigated defects and atomic diffusion in solid Li$_3$N using ab initio MD simulations. Wengert et al. [27] have presented the results of their ab initio MD simulations of the ionic conduction in Li$_{2-2x}$Mg$_{1+x}$Si. In these studies, the dynamic properties of the mobile ions, such as diffusion coefficients and atomic trajectories, have been discussed. More recently, electronic band
structure calculations have been carried out [28–30] to explain the high ionic conductivity in silver-ion conductors.

In the present article, we describe the method of ab initio MD simulations to investigate the atomic dynamics and the electronic states in the superionic conductors. We will discuss the microscopic mechanism of the high mobility of the mobile ions in two typical superionic conductors, CuI [31] and Ag2Se [32]. In CuI, the mobile Cu ions stay at two possible sites, tetrahedral and octahedral sites, in the fcc sublattice formed by the immobile I ions. Although the tetrahedral sites are energetically preferable, the mobile Cu ions must pass through an octahedral site when they migrate between two tetrahedral sites. On the other hand, the immobile Se ions in Ag2Se form the bcc lattice, which consists of the tetrahedron cages only. The mobile Ag ions migrate directly between two tetrahedral sites, and their diffusion mechanism could be different from that for Cu ions in CuI. It is, therefore, worth while comparing the diffusion mechanism of the mobile ions in these materials.

To investigate the bonding nature around the mobile ions, we will utilize the population analysis [33, 34] by expanding the electronic wavefunctions in an atomic orbital basis set. The population analysis describes intuitively the electronic structure of not only molecules but also disordered condensed systems in terms of chemical concepts [35]. We will give a detailed description of a recent development [35, 71, 72] of the formulation of the population analysis as well as the results for the superionic conductors.

II. Ab initio MD technique

The recent remarkable progress in theoretical studies of electronic states of condensed matter makes it possible to combine the electronic structure calculation and the MD simulation [36, 37], which is often called ab initio or first-principles MD simulation method. By this method, we can take into account of both the atomic dynamics and the electronic states at the same time from first principles.

The electronic structure of a physical system is calculated by the density functional theory (DFT) [38, 39]. In the Kohn-Sham formulation [40] of the DFT, the energy of the system is expressed as a functional of atomic positions \{R_i\} and one-electron wave functions (or Kohn-Sham orbitals) \{\psi_m\} in the atomic unit:

\[
E(\{\psi_m\}, \{R_i\}) = T_s[\rho] + \sum_m f_m \int \psi_m^*(r)V_{\text{ion}}(r)\psi_m(r)dr \\
+ \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r-r'|}drdr' + E_{xc}[\rho] + \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|R_i - R_j|},
\]

where \(T_s[\rho]\) is the kinetic energy of a noninteracting electron gas in its ground state with the number density \(\rho(r)\) of valence electrons, \(f_m\) an occupation
number of $m$th electronic state, $V_{\text{ion}}(r)$ an electron-ion interaction potential, $E_{\text{xc}}[\rho]$ the exchange-correlation energy functional, and the last term is the electrostatic energy between ions with valence $\{Z_i\}$. The valence electron number density $\rho(r)$ is calculated as

$$\rho(r) = \sum_m f_m |\psi_m(r)|^2 \quad .$$

(2)

The ground-state energy of the system, with given atomic positions $\{R_i\}$, is obtained by minimizing $E[\{\psi_m\}, \{R_i\}]$ with respect to $\{\psi_m(r)\}$, subjected to orthonormality constraints,

$$\int \psi_m^*(r) \psi_n(r)\, dr = \delta_{mn} \quad .$$

(3)

This minimization leads to the following eigenvalue equations (the Kohn-Sham equations),

$$\hat{H}_m \psi_m(r) = \varepsilon_m \psi_m(r) \quad .$$

(4)

with the eigenvalue $\varepsilon_m$ for the $m$th electronic state. The Kohn-Sham Hamiltonian $\hat{H}$ is defined through

$$\hat{H}_m \psi_m(r) = \left( -\frac{1}{2} \nabla^2 + V_{\text{ion}}(r) + V_{\text{H}}(r) + V_{\text{xc}}(r) \right) \psi_m(r) \quad ,$$

(5)

where $V_{\text{H}}(r)$ is the Hartree potential given by

$$V_{\text{H}}(r) = \int \frac{\rho(r')}{|r - r'|} \, dr' \quad ,$$

(6)

and $V_{\text{xc}}(r) = \delta E_{\text{xc}}[\rho]/\delta \rho$ is the exchange-correlation potential.

In the \textit{ab initio} MD simulations, we numerically integrate Newton’s equations of motion,

$$M_I \frac{d^2 R_I}{dt^2} = F_I \quad ,$$

(7)

where $M_I$ is the mass of $I$th ion, and the force $F_I$, acting on the $I$th ion, is calculated according to the Hellmann-Feynman theorem as
In most *ab initio* MD simulations, the local-density approximation (LDA) [41, 42] or the generalized gradient approximation (GGA) [43, 44] is used for the exchange-correlation energy $E_{xc}[\rho]$. The electronic wavefunctions are often expanded in the plane-wave (PW) basis set [45], because the formulae for the atomic forces as well as the total energy are simple. To save computational resources in the calculations with the PW basis sets, it is crucial to use a smooth pseudopotential for the interaction $V_{\text{ion}}(r)$ between the valence electrons and ion cores. By recent developments of the soft norm-conserving [46, 47] and the ultrasoft [48] pseudopotentials, the PW method combined with the pseudopotential approximation becomes one of the most popular methods for the electronic structure calculations.

In the pioneering theory invented by Car and Parrinello [36] for the *ab initio* MD simulations, a fictitious dynamics is assumed for the time evolution of the electronic wavefunctions. In contrast to this, we minimize the Kohn-Sham energy functional at each MD step using an iterative scheme based on preconditioned conjugate-gradient method [49–54]. This minimization of the energy functional guarantees the real dynamics of ions within the Born-Oppenheimer approximation, which separates the degrees of freedom of ions and electrons. A flowchart of this scheme for the *ab initio* MD simulations is shown in Fig. 1. First, the coordinates $\{R_i\}$ and the velocities $\{V_i\}$ of atoms are given as an initial condition. For this atomic configuration $\{R_i\}$, the energy functional $E[\{\psi_m\}, \{R_i\}]$ is minimized by the iterative scheme, and we obtain the quantum mechanical atomic forces. This minimization method consists of the following steps:

1. Calculation of the electronic potentials (the electron-ion interaction potential $V_{\text{ion}}(r)$, the Hartree potential $V_H(r)$ and the exchange-correlation potential $V_{xc}(r)$);
2. Unitary transformation of $\{\psi_m\}$ to make the corresponding Hamiltonian matrix diagonal;
3. Iterative improvement of $\{\psi_m\}$ so as to minimize the expectation value of Hamiltonian for each electronic state (to accelerate the convergence, the gradient vector for each state is preconditioned [49]);
4. Calculation of $\rho (r)$ using the updated $\{\psi_m\}$ and mixing it with the electronic densities at previous steps [55].
These steps are repeated until the self-consistency is achieved within an error tolerance. To obtain new coordinates and velocities at the next time step, the Newton’s equations of motion are solved using the atomic forces thus obtained. For this numerical integration, Nosé-Hoover thermostat technique [56, 57] is often used to generate the canonical ensemble, via the explicit reversible integrators [58, 59]. The initial charge density at each MD step is estimated by extrapolating the charge densities at the previous MD steps [53], and the initial wave functions are estimated from the wave functions at the previous MD steps by means of subspace diagonalization [51]. The charge extrapolation and the subspace diagonalization are very important ingredients in the \textit{ab initio} MD techniques to obtain a faster convergence of the total energy.

III. Atomic dynamics and chemical properties of superionic conductors

In this section, we elucidate the atomic dynamics and the electronic states in the superionic phases of CuI and Ag$_2$Se by the \textit{ab initio} MD simulation method described in the preceding section. We detail the methods and the techniques to analyze the simulation data, as well as the results and the physical conclusions.
A. Numerical details

The electronic structures are calculated within the framework of the DFT, in which the GGA [43] is used for the exchange-correlation energy $E_{xc}[\rho]$. The ultrasoft pseudopotentials [48, 60] are used for the interaction $V_{\text{ion}}(r)$ between the valence electrons and the ion cores. The valence-electron configurations of atoms Cu($3d^{10}4s^{1}4p^{0}$), I($5s^{2}5p^{5}5d^{0}$), Ag($4d^{10}5s^{1}5p^{0}$), and Se($4s^{2}4p^{3}4d^{0}$) are used in generating the pseudopotentials. We use systems of 64 (32Cu+32I) atoms for CuI and 162 (108Ag+54Se) atoms for Ag$_2$Se in cubic supercells with the periodic boundary conditions. The time steps used in the numerical integration of the equations of motion with the Nosé-Hoover thermostat technique are 2 and 2.4 fs for CuI and Ag$_2$Se, respectively. The temperatures are set to be 700 K for CuI and 500 K for Ag$_2$Se, which are above respective superionic transition temperatures $T_c = 681$ K (CuI) and 416 K (Ag$_2$Se). The number densities of atoms ($0.0328\text{Å}^{-3}$ for CuI and $0.0461\text{Å}^{-3}$ Ag$_2$Se) are taken from the experiments. The plane-wave cutoff energy $E_{\text{cut}}$ for the electronic wavefunctions and $E_{\text{dens}}$ for the electron number density are $E_{\text{cut}} = 17$ ry. and $E_{\text{dens}} = 120$ ry. for CuI, and $E_{\text{cut}} = 14.5$ ry. and $E_{\text{dens}} = 80$ ry. for Ag$_2$Se. The $\gamma$ point is used for the Brillouin zone sampling. The MD simulation for CuI begins with the zinc-blende structure. In the initial atomic configuration for the simulations of Ag$_2$Se, the immobile Se ions are placed at the lattice positions of the bcc structure, while the mobile Ag ions occupy the tetrahedral sites randomly. Note that the number of the tetrahedral sites is three times larger than that of Ag ions. The quantities of interest are obtained by averaging over 5 ps after the initial equilibration taking 6 ps.

B. Mean-square displacements

The mean square displacement (MSD) $\phi_\alpha(t)$ for $\alpha$-type ion is defined as

$$
\phi_\alpha(t) = \frac{1}{N_\alpha} \sum_{\mathbf{r} \in \alpha} \left\langle |\mathbf{R}_\mathbf{r}(t + t_0) - \mathbf{R}_\mathbf{r}(t_0)|^2 \right\rangle_{t_0},
$$

where $N_\alpha$ is the number of $\alpha$-type ion and the brackets $\langle \ldots \rangle_{t_0}$ mean the average over the time $t_0$. Figure 2 shows the MSD’s for the superionic phases of CuI and Ag$_2$Se. The solid and dashed lines display the MSD’s for the anions and the cations, respectively, in these materials. The MSD’s for Cu and Ag ions have a finite slope, while those for I and Se ions remain almost constant at large time, which clearly shows that the superionic behavior of CuI and Ag$_2$Se is successfully reproduced by the ab initio MD simulations. The diffusion coefficients $D_\alpha$ for the mobile ions are obtained from the MSD’s as...
\[ D_\alpha = \lim_{t \to \infty} \frac{1}{6t} \phi_\alpha(t). \]  

For CuI and Ag\textsubscript{2}Se, \( D_{\text{Cu}} \) and \( D_{\text{Ag}} \) are estimated to be \( 4 \times 10^{-5} \) and \( 1 \times 10^{-5} \) cm\textsuperscript{2}/s, respectively, which are in reasonable agreement with the experimental values \([61, 62]\).

**Figure 2.** Mean square displacements \( \phi_\alpha(t) \) in the superionic phases of CuI and Ag\textsubscript{2}Se. The solid and dashed lines show \( \phi_\alpha(t) \) for anions (I and Se) and cations (Cu and Ag), respectively.

**C. Static structure**

The total static structure factor \( S(k) \) is defined as

\[
S(k) = \frac{\sum_\alpha \sum_\beta f_\alpha(k)f_\beta(k)\sqrt{c_\alpha c_\beta} S_{\alpha\beta}(k)}{\sum_\alpha f_\alpha^2(k)c_\alpha},
\]

where \( f_\alpha(k) \) and \( c_\alpha \) are the X-ray scattering factor and the atomic fraction, respectively, for \( \alpha \)-type atom. So one can compare the calculated \( S(k) \) defined by eq.(11) with the experimental results obtained by the X-ray diffraction technique. If \( f_\alpha(k) \) is replaced by the neutron scattering length \( b_\alpha \) in eq.(11), one can obtain the structure factor corresponding to the neutron diffraction measurements. \( S_{\alpha\beta}(k) \) are the Ashcroft-Langreth partial structure factors \([63]\) defined by
In Fig. 3, we show the total structure factors $S(k)$ obtained by \textit{ab initio} MD simulations for the superionic phases of CuI and Ag$_2$Se. It is seen that $S(k)$'s have sharp peaks with an oscillatory broad background. This behavior of $S(k)$ is in good agreement with that observed in the X-ray diffraction experiments [64]. The partial structure factors $S_{\text{SeSe}}(k)$, $S_{\text{AgAg}}(k)$ and $S_{\text{AgSe}}(k)$ in the superionic phase of Ag$_2$Se are displayed in Fig. 4. As shown in Fig. 4(a), $S_{\text{SeSe}}(k)$ consists of several Bragg peaks, which give the sharp peaks in the total $S(k)$. The reflection indices $(hkl)$ can be assigned to the Bragg peaks, and it is obvious that the immobile Se ions form the bcc lattice. On the other hand, $S_{\text{AgAg}}(k)$ has only a broad profile as displayed in Fig. 4(b), which reflects the disordered structure of Ag ions. Since $S_{\text{AgSe}}(k)$ has sharp dips corresponding to the $(110)$, $(310)$, and $(222)$ reflections, the Bragg peaks for these reflection indices do not appear in the total $S(k)$.

The partial pair distribution functions $g_{\alpha\beta}(r)$ are defined by

$$
g_{\alpha\beta}(r) \Delta r = \frac{1}{\rho_{\beta}} \frac{n_{\alpha\beta}(r)}{4\pi r^2} \Delta r \ .
$$
Figure 4. Partial structure factors $S_{\alpha\beta}(k)$ for $\alpha-\beta = \text{Se-Se (a), Ag-Ag (b) and Ag-Se (c)}$ in the superionic phase of Ag$_2$Se [32].

where $\rho_\beta$ is the number density of $\beta$-type ions, and $\langle n_{\alpha\beta}(r)\rangle_\alpha \Delta r$ is the average number of $\alpha$-type ions around an $\alpha$-type ions at the distance between spherical shells of radii $r$ and $r + \Delta r$. The brackets $\langle \cdots \rangle_\alpha$ denotes the average over all $\alpha$-type ions.

Figure 5 shows $g_{\alpha\beta}(r)$ obtained by the *ab initio* MD simulations for the superionic phase of CuI. The position of the first peak of $g_{ii}(r)$ is about 4.3 Å, while that of $g_{\text{CuCu}}(r)$ is about 2.6 Å. A remarkable feature exhibited in $g_{\alpha\beta}(r)$ is that the position of the first peak of the cation-cation correlation $g_{\text{CuCu}}(r)$ is not close to that of the anion-anion correlation $g_{ii}(r)$ but that of the cation-anion correlation $g_{\text{CuI}}(r)$ in spite of the correlation between the same type of ions. Similarly, this peculiarity is seen in the superionic phase of Ag$_2$Se; the position of the first peak of $g_{\text{AgAg}}(r)$ is almost the same as that of $g_{\text{AgSe}}(r)$ as displayed in Fig. 6. Since this feature is also observed experimentally for the superionic phase of AgI [65] as well as the molten phases of several superionic compounds, such as CuI [66], Ag$_2$Se, Ag$_2$Te [67, 68] SrCl$_2$, BaCl$_2$ [69, 70], it is expected that this feature is widely seen in most materials which exhibit the superionic behavior, and may relate to the physical origin of the appearance of the superionic phases. It has been found from the population analysis [31,32]
Figure 5. Partial pair distribution functions $g_{\alpha\beta}(r)$ for $\alpha-\beta = \text{I-I (a), Cu-I (b) and Cu-Cu (c)}$ in the superionic phase of CuI [31].

Figure 6. Partial pair distribution functions $g_{\alpha\beta}(r)$ for $\alpha-\beta = \text{Se-Se (a), Ag-Se (b) and Ag-Ag (c)}$ in the superionic phase of Ag$_2$Se [32].

that the short cation-cation distance originates from an attractive interaction between cations due to the hybridization of atomic orbitals. A related discussion will be given in the following subsections.

**D. Electronic density of states**

The total electronic density of states (DOS) $D(E)$ is defined by
\[ D(E) = \left\{ \sum_n \delta(E - \varepsilon_n) \right\}, \]

where \( \varepsilon_n \) is the eigenenergy of the \( n \)th electronic state. The total DOS \( D(E) \) is rewritten as a sum of the partial DOS \( D_{\alpha}(E) \) for \( \alpha \)-type ions;

\[ D(E) = \sum_{\alpha} c_{\alpha} D_{\alpha}(E), \]

where \( c_{\alpha} \) is the atomic fraction of \( \alpha \)-type ions. Moreover, \( D_{\alpha}(E) \) is decomposed into the partial DOS \( D^l_{\alpha}(E) \) associated with the atomic orbitals with the angular momentum \( l \) on \( \alpha \)-type ions;

\[ D_{\alpha}(E) = \sum_l D^l_{\alpha}(E). \]

Using the weight \( w^l_{\alpha}(n) \) of the atomic orbitals with the angular momentum \( l \) on \( \alpha \)-type ions, \( D^l_{\alpha}(E) \) are defined by

\[ D^l_{\alpha}(E) = \left\{ \sum_n w^l_{\alpha}(n) \delta(E - \varepsilon_n) \right\}. \]

The weights \( w^l_{\alpha}(n) \) are calculated by expanding the electronic wavefunctions in the atomic orbitals on each ion (see the later subsection), and are normalized as

\[ \sum_{\alpha, l} c_{\alpha} w^l_{\alpha}(n) = 1 \]

to satisfy eqs.(15) and (16).

Figure 7 shows the DOS's in the superionic phase of CuI. The total DOS \( D(E) \) is shown in Fig. 7(a). The partial DOS's \( D_{\alpha}(E) \) for I and Cu ions are shown in Figs. 7(b) and 7(c), respectively. The origin of the energy is taken to be the Fermi level \( (E_F = 0) \). In \( D_{I}(E) \), the electronic states around \(-13 \) eV are \( s \)-like in character, and those between \(-7 \) and \( 0 \) eV are \( p \)-like.

The large peak around \(-2 \) eV in \( D_{Cu}(E) \) originates from \( 3d \) electronic states. It is evident that the \( 3d \) electronic states of Cu ions hybridize with the \( 5p \) states of I ions with an energy range from \(-7 \) to \( 0 \) eV.

The DOS's in the superionic phase of Ag\(_2\)Se are shown in Fig. 8, where the partial DOS \( D^l_{\alpha}(E) \) associated with the atomic orbitals with the angular momenta of \( l = 0, 1 \) and 2 for \( \alpha = \text{Se} \) and Ag, as well as the total DOS \( D(E) \), are displayed. It is seen that the \( 4s \) states of Se atoms give the peak around \(-13 \) eV of \( D(E) \). The electronic states from \(-6 \) to \( 0 \) eV consists mainly of the \( 4d \) states of Ag atoms and the \( 4p \) states of Se atoms, which suggests that the \( 4d-4p \)
Figure 7. Total electronic density of states $D(E)$ (a) and partial electronic densities of states $D_{\alpha}(E)$ for I (b) and Cu (c) ions in the superionic phase of CuI [31]. The origin of the energy is taken at the Fermi level ($E_F = 0$).

Figure 8. Total electronic density of states $D(E)$ (a), and partial electronic densities of states $D_{\alpha}(E)$ for $\alpha =$ Se (b) and Ag (c) ions in the superionic phase of Ag$_2$Se [32]. $D_{\alpha}(E)$ are shown by the solid, dashed and dotted lines for the atomic orbitals with angular momentum of $l = 0, 1$ and 2, respectively. The origin of the energy is taken at the Fermi level ($E_F = 0$).
hybridization occurs between Ag and Se atoms similar to the 3d-5p hybridization in CuI. As shown in the insets of Fig. 8(b) and 8(c), the 4d states of Se atoms and the 5s and 5p states of Ag ions are occupied by some electrons in the same energy range of the 4d-4p hybridization. Note that the 4d-4p hybridization in Ag2Se and also the 3d-5p hybridization in CuI give only a small contribution to the chemical bonding between cations and anions, since a cancellation between contributions from the bonding and anti-bonding hybridized states takes place. The chemical properties are mainly determined by the hybridizations with excited states, such as the 5s and 5p states of Ag ions and the 4d states of Se ions.

E. Population analysis
In this subsection, we describe the method of the population analysis [33, 34], which has been originally applied to the analysis of the electronic structure of molecules obtained with a localized basis set, such as Gaussian basis set, utilized mainly in the field of quantum chemistry. The population analysis is a useful tool to investigate the bonding nature of high-temperature materials, since it describes intuitively the electronic structure of not only molecules but also disordered condensed systems in terms of chemical concepts [35]. Here we explain a formulation [71] of the analysis for the plane-wave (PW) basis set with the ultrasoft pseudopotentials.

To project the self-consistent wavefunctions $\psi_n(r)$ obtained with the PW basis into the subspace generated by the atomic basis $\{\phi_\mu\}$, the projection operator $\hat{P}$ is defined as [35, 71, 72]

$$\hat{P} = \sum_{\mu,\nu} |\phi_\mu\rangle S_{\mu\nu}^{-1} \langle \phi_\nu | \hat{s},$$

where $S_{\mu\nu} = \langle \phi_\mu | \hat{s} | \phi_\nu \rangle$, and $\hat{s} = 1 + \sum_{\mu\nu} \{ \int dr \, q_{\mu\nu}(r) \} |\beta_\mu\rangle \langle \beta_\nu|$ with $\beta_\mu(r)$ and $q_{\mu\nu}(r)$ being the localized functions and the augmentation functions, respectively, in the ultrasoft pseudopotentials [48]. Note that the formulation for the norm-conserving pseudopotentials is obtained if $\hat{s} = 1$. The projected wavefunctions $\chi_n(r)$ are obtained by operating $\hat{P}$ on $\psi_n(r)$ as

$$|\chi_n\rangle = \hat{P} |\psi_n\rangle = \sum_\mu |\phi_\mu\rangle C_{\mu n},$$

with
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\[ C_{\mu n} = \sum_{\nu} S_{\mu \nu}^{-1} \langle \phi_{\nu} | \hat{\mathbf{s}} | \psi_{n} \rangle . \]  

(21)

Generally \( \psi_{n}(\mathbf{r}) \) are not orthonormalized;

\[ R_{nm} \equiv \langle \chi_{n} | \hat{\mathbf{s}} | \chi_{m} \rangle \neq \delta_{nm} . \]  

(22)

To ensure the charge conservation, the dual of \( \chi_{n}(\mathbf{r}) \) is introduced as \[35\]

\[ | \chi^{\pi} \rangle = \sum_{m} | \chi_{m} \rangle R_{mn}^{-1} = \sum_{\mu} | \phi_{\mu} \rangle C_{\mu n} \]  

(23)

with

\[ C_{\mu n} = \sum_{m} C_{\mu m} R_{mn}^{-1} , \]  

(24)

so that

\[ \langle \chi^{\pi} | \hat{\mathbf{s}} | \chi_{m} \rangle = \sum_{\mu \nu} C_{\mu n}^{\nu} S_{\mu \nu} C_{\nu m} = \delta_{nm} . \]  

(25)

With respect to the \( n \)th electronic state, the partial gross atomic population \( N^{(n)}_{\mu} \) associated with the \( \mu \)th atomic basis function and the partial overlap population \( O^{(n)}_{\mu \nu} \) associated with the \( \mu \)th and \( \nu \)th atomic basis functions are defined as \[33\]

\[ N^{(n)}_{\mu} = \sum_{\nu} C^{\nu n}_{\mu} S_{\nu \mu} C_{\mu n} \]  

(26)

and

\[ O^{(n)}_{\mu \nu} = \frac{1}{2} \left( C^{\mu n}_{\nu \mu} S_{\nu \mu} C_{\mu n} + C^{\nu n}_{\mu \nu} S_{\nu \mu} C_{\mu n} \right) , \]  

(27)

respectively. The gross atomic population \( N_{i} \) on \( i \)th atom and the overlap population \( O_{ij} \) for a pair of \( i \)th and \( j \)th atoms are obtained by summing \( N^{(n)}_{\mu} \) and \( O^{(n)}_{\mu \nu} \), respectively, as follows
where \( f_n \) is the electronic occupation number of the \( n \)th electronic state. The sum associated with the atomic orbitals, \( \sum_{\mu(i,j)} \), is taken on \( i \)th atom. \( N_i \) is decomposed into the angular momentum dependent partial gross atomic population \( N_{i}^{l} \) as

\[
N_i = \sum_{l} N_{i}^{l}
\]  

(30)

with

\[
N_{i}^{l} = \sum_{\mu(i,l)} f_{n} N_{\mu}^{(n)}
\]  

(31)

where \( \sum_{\mu(i,l)} \) means that the sum is taken associated with \( \mu \) related to \( i \)th atom and the angular momentum \( l \). A similar decomposition is also possible for \( O_{ij} \).

The weights \( w_{\alpha}(n) \) in eq. (17) are calculated as

\[
w_{\alpha}^{l}(n) = \sum_{i \in \alpha} \sum_{\mu(i,l)} N_{\mu}^{(n)}
\]  

(32)

To measure the ionicity of each atom, it is beneficial to define the gross charge \( Q_i \) as [33]

\[
Q_i = N_{i}^{0} - N_i
\]  

(33)

where \( N_{i}^{0} \) is the total number of valence electrons in the ground state of the free neutral atom. Also, we define \( O_i \) as the sum of the overlap population \( O_{ij} \) with respect to the neighboring \( j \)th atoms as

\[
O_i = \sum_{j} O_{ij}
\]  

(34)
to estimate the degree of interaction on $i$th atom due to the overlap of the atomic orbitals with its neighboring atoms.

In the following two subsections, we describe the chemical properties of Ag ions in the superionic phase of Ag$_2$Se investigated by the population analysis. For the superionic phase of CuI, we have also investigated the time evolution of bonding nature around a Cu ion [31] by utilizing the population analysis. For the discussion on the chemical properties in CuI, refer to the article by Prof. M. Aniya in this book.

### F. Chemical properties of mobile ions

The bcc sublattice formed by the immobile Se ions consists of Se$_4$ tetrahedra, and the mobile Ag ions migrate directly between two tetrahedral sites. Figure 9 shows the diffusive motion of the focused Ag ion. At $t = 0$ ps, it occupies a tetrahedral site, and goes toward a neighboring tetrahedral site through a triangle formed by three Se ions denoted as ‘Se’ in Figs. 9(b) and 9(c), where the focused Ag ion is denoted as ‘Ag’. Figure 9(a) shows the time evolution of the distance $d_i$ between the Ag ion and the triangle. $d_i$ is defined to be positive and negative, when the Ag ion is on the inside and outside of the tetrahedron occupied by the Ag ion at $t = 0$ ps, respectively. As shown in Fig. 9(a), $d_i$ changes its sign at approximately $t = 0.5$ ps, which means that the Ag ion moves toward the neighboring tetrahedral site. Figures 9(b) and 9(c) display the atomic configurations around the Ag ion at $t = 0.1$ and 0.9 ps, respectively.

![Figure 9](image)

**Figure 9.** (a) Time evolution of the distance $d_i$ between the Ag ion and the triangle formed by three Se ions. (b) Atomic configuration around the Ag ion at $t = 0.1$ ps. The focused triangle is formed by three Se ions denoted as ‘Se’. (c) Atomic configuration around the Ag ion at $t = 0.9$ ps [32].
The time evolutions of $Q_i$ and $O_i$ of the focused Ag ion are shown in Fig. 10. The time $t$ in the horizontal axis corresponds to that in Fig. 9(a). From Fig. 10, it seems that $Q_i$ and $O_i$ keep larger and smaller values, respectively, than the respective average values over all Ag ions during the migration around $t = 0.5$ ps, as indicated by the large circles in the figures. These results may suggest that the ionicity and the strength of the chemical bonding of the Ag ions change accompanied with the diffusive motion, as was seen in the superionic phase of CuI [31]. In the case of CuI, the ionicity of the Cu ions at the octahedral sites is larger than that of the Cu ions at the tetrahedral sites, and the chemical bonding around Cu ions weakens when they pass through the octahedral site during the migration between the neighboring tetrahedral sites.

![Figure 10](image)

**Figure 10.** Time evolutions of (a) the gross charge $Q_i$ and (b) the sum of overlap population $O_i$ of the focused Ag ion. Time $t$ in the horizontal axis corresponds to that for Fig. 9(a). The small circles show $Q_i$ and $O_i$, while the solid lines show the average values over all Ag ions.

In Figs. 9 and 10, an example of the time evolution of the chemical bonding around a Ag ion is displayed. However, it is hard to draw a physically meaningful conclusion from the time evolutions of $Q_i$ and $O_i$, since they fluctuate largely with time. In order to get more reliable picture for the chemical properties of Ag ions, we take averages of $Q_i$ and $O_i$ as a function of position of Ag ions in tetrahedra formed by four Se ions. The position of $i$th Ag ion is simply measured by a parameter $u_i$ defined as
where $R_{iG}$ is the distance between the position of $i$th Ag ion and the position of the center of gravity of the tetrahedron occupied by the Ag ion, and $R_{iM}$ the distance between the $i$th Ag ion and the triangle face nearest to the Ag ion (see Fig. 11). From this definition, $u_i$ is zero when the Ag ion resides in the center of tetrahedron, while $u_i$ becomes unity when the Ag ion is on one of the triangle faces.

![Figure 11. Schematic diagram of a tetrahedron formed by four Se ions. $R_i$ is the position of Ag ion inside the tetrahedron. $R_G$ denotes the center of gravity of the tetrahedron. $R_M$ is the intersection between the triangle face ABC and the perpendicular line to the face, which passes through the Ag ion. The position of Ag ion is measured by a parameter $u_i = R_{iG} / (R_{iG} + R_{iM})$ with $R_{iG} = |R_i - R_G|$ and $R_{iM} = |R_i - R_M|$.](image)

Figures 12(a)~12(d) show the averaged gross populations $N_{Ag}(u) = \sum_i N^i_{Ag}(u)$ and $N^i_{Ag}(u)$. As expected from Fig. 10(a), the averaged total gross populations $N_{Ag}(u)$ decreases slightly with increasing $u$. This means that the ionicity becomes larger compared with that at the vicinity of the center of the tetrahedron, when the Ag ions pass through the triangle faces. It is seen from Fig. 12(c) that the reduction of $N_{Ag}(u)$ mainly comes from the decrease in $N^p_{Ag}(u)$. Also $N^d_{Ag}(u)$ decreases slightly with increasing $u$ while $N^s_{Ag}(u)$ increases, as shown in Figs. 12(d) and 12(b), respectively. Figures 12(e) ~ 12(g) show the averaged overlap populations $O_{Ag}(u) = \sum_\alpha O_{Ag-\alpha}(u)$ and $O_{Ag-\alpha}(u)$. Unexpectedly, the averaged total overlap population $O_{Ag}(u)$ is almost unchanged with $u$ as shown in Fig. 12(e). It is, however, seen from Figs. 12(f) and 12(g) that the averaged partial overlap populations $O_{Ag-\alpha}(u)$ is
largely changed. From the fact that $O_{\text{Ag-Se}}(u)$ decreases with increasing $u$, we see that the covalent-like interactions between Ag and Se ions become weaker when Ag ions migrate between the tetrahedra. The increase of $O_{\text{Ag-Ag}}(u)$ at larger $u$ indicates attractive interactions between Ag ions due to the overlap of the atomic orbitals near the triangle faces.

Figure 12. Averaged total gross population $N_{\text{Ag}}(u) = \sum_i N_{\text{Ag}}^i(u)$ (a), and averaged partial gross populations $N_{\text{Ag}}^l(u)$ for $l = s$ (b), $p$ (c), and $d$ (d) as a function of the parameter $u$. Averaged total overlap population $O_{\text{Ag}}(u) = \sum_{\alpha} O_{\text{Ag-\alpha}}(u)$ (e), and averaged partial overlap populations $O_{\text{Ag-\alpha}}(u)$ for $\alpha = \text{Se}$ (f) and Ag (g) as a function of the parameter $u$.

G. Displacement-correlation function

The interactions between two Ag ions may trigger some correlations between them in their diffusive motion near the triangle faces. To investigate such a collective motion between Ag ions, we calculate the displacement-correlation functions (DCF) $\zeta(t)$ defined as

$$\zeta(t) = \langle \Delta R_i(t) \cdot \Delta R_j(t) \rangle,$$  \hspace{1cm} (36)
where $\Delta R_i(t) = R_i(t_0 + t) - R_i(t_0)$ with $R_i(t)$ being the position of $i$th ion at a time $t$. The brackets mean the averages over both the time $t_0$ and atomic pairs ($i, j$) with $i, j \in \text{Ag}$. In the calculation, Ag pairs with $|R_i(t_0) - R_j(t_0)| < R$ are chosen. We use $R = 3.2$ Å, which is determined from the first-peak position of $g_{\text{AgAg}}(r)$. The solid line in Fig. 13(a) shows the time evolution of $\zeta(t)$ for 2 ps. Although $\zeta(t)$ increases with $t$, its increasing rate is not so large, which may suggest that Ag ions exhibit only a weak collective motion with their neighboring Ag ions. However, $\zeta(t)$ includes a correlation between two Ag ions which do not diffuse and remain in their respective tetrahedra for a while.

![Figure 13](image.png)

**Figure 13.** Displacement-correlation functions (DCF) (a) $\zeta(t)$ and $\overline{\zeta}(t)$, and (b) $\zeta(t)/t^2$ and $\overline{\zeta}(t)/t^2$ [32].

Since we are interested in the correlation between diffusing Ag ions, we calculate the DCF $\overline{\zeta}(t)$ for atomic pairs ($i, j$) that satisfy the conditions $|\Delta R_i(T)| > \overline{R}$ and $|\Delta R_j(T)| > \overline{R}$, as well as the condition $|R_i(t_0) - R_j(t_0)| < \overline{R}$, where $T = 2.0$ ps and $R$ is the distance between the neighboring tetrahedral sites. As displayed by the dashed line in Fig. 13(a), $\overline{\zeta}(t)$ increases largely with increasing $t$. It is concluded from these results that Ag ions exhibit a remarkable collective motion with their neighbor Ag ions when they migrate.
between the neighboring tetrahedral sites. From the definition of the DCF, it would increase as \( t^2 \), if two Ag ions migrated together for a time interval \( t \). It is, therefore, reasonable to divide the DCF by \( t^2 \) to estimate the time scale of the collective motion between Ag ions. Figure 13(b) shows \( \zeta(t)/t^2 \) and \( \bar{\zeta}(t)/t^2 \). From this figure, it is found that \( \zeta(t)/t^2 \) and \( \bar{\zeta}(t)/t^2 \) have finite values at \( t = 0 \) ps, and have maxima at about \( t = 0.2 \) ps. This time interval might be considered as a delay time to start the collective motion between a pair of Ag ions. That is, each Ag ion might need time of about 0.2 ps to feel the diffusing motions of neighboring Ag ions. After this time, the correlation between Ag ions gradually decreases with increasing time.

**IV. Summary**

In this article, we have detailed the method of *ab initio* molecular-dynamics simulations, and have demonstrated that the superionic behavior in CuI and Ag\(_2\)Se is successfully reproduced from first principles. It is shown that the calculated static structure factor consists of the sharp Bragg peaks with an oscillatory broad background, which is in agreement with the experimental observations. A remarkable feature exhibited in the partial pair distribution functions is that the nearest-neighbor distance between cations is close to that between cations and anions in spite of the correlation between the same type of ions. The chemical properties in these materials have also been described in detail based on the population analysis. It is found that the chemical properties of the mobile ions vary accompanied with the diffusive motion. The mobile Ag ions in the superionic phase of Ag\(_2\)Se interact with their neighboring Ag ions through the attractive interaction due to the overlap of the atomic orbitals, when they diffuse near the triangle faces of the tetrahedra formed by four Se ions. It is also shown from the displacement-correlation function that Ag ions exhibit a collective motion with their neighbor Ag ions. In conclusion, it is important to investigate the electronic states in the superionic conductors together with the disordered atomic structure to consider the high ionic conductivity. For this purpose, the *ab initio* molecular-dynamics simulations are useful and powerful, although we must be aware of their limitations coming from the approximations in the density-functional theory.

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References