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Model for the charge transfer of ionic materials

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A model based on the Hartree-Fock-Slater theory is proposed for the charge transfer in ionic materials. Application of this model to some diatomic molecules is demonstrated. Most available experimental data are well reproduced.

I. INTRODUCTION

In this paper we propose a simple method for obtaining an amount of charge transfer (CT) for diatomic molecules. This method is based on an expansion of the total energy of an atom with respect to an occupation number, which has been developed by Slater.[1] The point to be emphasized in our method is that only atomic quantities for an isolated atom which are calculated from the Hartree-Fock-Slater (HFS) theory[1] are used. This method is also applicable to prediction of CT in ionic crystals. A similar problem has been addressed by Watson *et al.*[2] Their results of CT for ionic crystals are somewhat smaller than the values normally attributed to these crystals. They have suggested that this discrepancy will be improved by inclusion of the Madelung effect. The present work is along this suggestion in some sense.

II. THEORY

Let us consider a diatomic molecule, AB. The total energy E_{mol} for the molecule can be expressed as

$$E_{\mathrm{mol}}=\langle E\rangle_A+\langle E\rangle_B+E_C+E_R+E_d\ , \tag{1}$$

where E_R and E_d are repulsive and dipole-dipole attractive energies, respectively; they do not depend on the CT for A and B atoms, δq_A and δq_B. Here, δq_i $(i=A,B)$ is defined by $\sum_{n,\lambda}\omega_{n\lambda}^{(i)}-Z_i$, where Z_i is the atomic number of an i atom and $\omega_{n\lambda}^{(i)}$ is the occupation number for the orbital specified by $n\lambda$. E_C is the Coulomb energy due to the CT, which is given by $\alpha_M^{(\mathrm{mol})}\delta q_A\delta q_B/R$, where R is the minimum interatomic distance in a.u. and $\alpha_M^{(\mathrm{mol})}$, which corresponds to the Madelung constant in crystals, is usually taken to be 2 in the case of diatomic molecules. $\langle E\rangle_i$ is the total energy of electrons for an i atom $(i=A,B)$. In the framework of HFS theory, it is approximated as follows:

$$\langle E\rangle_i=\langle E\rangle_i^0+\varepsilon_{\mathrm{CT}}^{(i)}\delta q_i+\tfrac{1}{2}\xi_{\mathrm{CT}}^{(i)}(\delta q_i)^2\ , \tag{2a}$$

$$\xi_{\mathrm{CT}}^{(i)}=\int\int d\mathbf{r}_1 d\mathbf{r}_2\,|\psi_{\mathrm{CT}}^{(i)}(\mathbf{r}_1)|^2\,|\psi_{\mathrm{CT}}^{(i)}(\mathbf{r}_2)|^2\frac{2}{|\mathbf{r}_1-\mathbf{r}_2|}-2\alpha_{\mathrm{ex}}^{(i)}\left[\frac{3}{8\pi}\right]^{1/3}\int d\mathbf{r}\,|\psi_{\mathrm{CT}}^{(i)}(\mathbf{r})|^4\rho_i(\mathbf{r})^{-2/3}\ , \tag{2b}$$

where $\langle E\rangle_i^0$ is the total energy of electrons for an isolated i atom, $\varepsilon_{\mathrm{CT}}^{(i)}$ and $\psi_{\mathrm{CT}}^{(i)}$ are , respectively, the one-electron energy level and the wave function for the orbital (CT orbital) which participates in CT, and ρ_i is the electron density for an i atom. These atomic values ($\varepsilon_{\mathrm{CT}}^{(i)}$, $\xi_{\mathrm{CT}}^{(i)}$, and ρ_i) for an isolated i atom are obtained from self-consistent-field (SCF) calculation following a prescription of Herman and Skillman[3] by use of Schwarz's exchange parameter α_{ex} (Ref. 4) optimized statistically. By using Eqs. (2), we can rewrite Eq. (1) in a more explicit form:

$$E_{\mathrm{mol}}=g_{\mathrm{mol}}+c_{\mathrm{mol}}\ , \tag{3a}$$

$$g_{\mathrm{mol}}=(\overline{\xi}_{\mathrm{mol}}-\alpha_M^{(\mathrm{mol})}/R)q^2(R)+\Delta\varepsilon q(R)\ , \tag{3b}$$

$$c_{\mathrm{mol}}=\langle E\rangle_A^0+\langle E\rangle_B^0+E_R+E_d\ , \tag{3c}$$

where $\overline{\xi}_{\mathrm{mol}}=(\xi_{\mathrm{CT}}^{(A)}+\xi_{\mathrm{CT}}^{(B)})/2$, $\Delta\varepsilon=\varepsilon_{\mathrm{CT}}^{(A)}-\varepsilon_{\mathrm{CT}}^{(B)}$, and $q(R)\equiv\delta q_A=-\delta q_B$. Here, it should be noted that c_{mol} does not depend on $q(R)$. The condition $(dE_{\mathrm{mol}}/dq\,|_{R=\mathrm{const}}=0)$ of the energy minimum, for a given R,

TABLE I. $\varepsilon_{n\lambda}$ and $\xi_{n\lambda}$ (in a.u.) for charge-transfer orbitals ($n\lambda$). α_{ex} is Schwarz's exchange parameter used in the calculation of $\varepsilon_{n\lambda}$ and $\xi_{n\lambda}$.

Atom	α_{ex}	Orbital ($n\lambda$)	$-\varepsilon_{n\lambda}$	$\xi_{n\lambda}$
Li	0.780 87	2*s*	0.392 472 5	0.390 707 8
Na	0.730 44	3*s*	0.360 374 9	0.365 360 0
K	0.720 72	4*s*	0.289 851 9	0.293 942 6
Rb	0.705 25	5*s*	0.270 077 1	0.274 966 6
Cs	0.7014[a]	6*s*	0.242 356 1	0.246 061 8
F	0.736 51	2*p*	0.996 847 9	1.535 641
Cl	0.722 77	3*p*	0.714 264 2	0.885 389 6
Br	0.705 76	4*p*	0.640 782 6	0.770 071 7
I	0.702[a]	5*p*	0.567 486 5	0.651 013 9

[a] Determined from extrapolation.

leads to the expression for CT, $q_{\mathrm{mol}}(R)$, for diatomic molecules,

$$q_{\mathrm{mol}}(R)=\frac{-\Delta\varepsilon}{2(\bar{\xi}_{\mathrm{mol}}-\alpha_M^{(\mathrm{mol})}/R)} . \tag{4}$$

This expression is very similar to that derived by Watson *et al.*,[2] apart from the term $\alpha_M^{(\mathrm{mol})}/R$.

The extension of diatomic molecules to crystals is very easy and is described in the Appendix.

The Madelung constant determined from the geometry of atoms should be modified from the usual value, when each ionized atom cannot be regarded as a point charge. Even in the case of diatomic molecules, it is a troublesome task to calculate the value of $\alpha_M^{(\mathrm{mol})}$, because SCF calculations for the ionized atom are required. This implies that in the case of crystals it is more difficult to take into account of a correction to the Madelung constant due to the spatial distribution of electrons. In order to avoid this difficulty, in the following we introduce an assumption on the variation of the Madelung constant with the distance between atoms.

Let us consider a situation that two atoms approach each other from a large distance, where the overlap (Δ) between CT orbitals vanishes, to a smaller distance R, where $\Delta(R)$ is nonzero. We can see that $\alpha_M^{(\mathrm{mol})}(R)$ for real molecules is smaller than 2 for a point charge, since the contribution of the electron-electron repulsive interaction to the Coulomb energy increases positively when $\Delta(R)$ becomes a finite value. This implies that $\alpha_M^{(\mathrm{mol})}(R)$ decreases with increasing $|\Delta(R)|$. From this qualitative behavior of $\alpha_M^{(\mathrm{mol})}(R)$, we shall *a priori* assume that $\alpha_M^{(\mathrm{mol})}(R)$ varies as $\alpha_M \exp[-|\Delta(R)|]$, where α_M stands for the Madelung constant for $\Delta(R)=0$. Using $\alpha_M^{(\mathrm{mol})}=2\exp[-|\Delta(R)|]$ in Eq. (4), we will calculate $q_{\mathrm{mol}}(R)$ for some diatomic molecules.

III. RESULTS

The calculated atomic quantities $\varepsilon_{n\lambda}$ and $\xi_{n\lambda}$ for CT orbitals ($n\lambda$) are listed for Li, Na, K, Rb, Cs, F, Cl, Br, and I atoms, together with the exchange parameter α_{ex}, in Table I. These energy levels $\varepsilon_{n\lambda}$ for CT orbitals were obtained from the SCF calculation by using Schwarz's ex-

TABLE II. Calculated (q_{mol}), Pauling's (q_{Paul}), and experimental (q_{expt}) charge transfer. Interatomic distance R (in a.u.) and overlap Δ between CT orbitals are also listed.

Molecule	R[a]	Δ	q_{mol}	q_{Paul}	q_{expt}
LiF	2.872	0.1003	0.907	0.895	0.908[b]
LiCl	3.834	−0.2314	0.718	0.623	0.730[b]
LiBr	4.101	0.2735	0.593	0.555	0.595[b]
LiI	4.520	−0.3244	0.435	0.430	0.548[b]
NaF	3.489	−0.093 48	0.743	0.910	
NaCl	4.4618	0.2033	0.682	0.668	0.750[b]
NaBr	4.7282	−0.2403	0.596	0.594	
NaI	5.1251	0.2860	0.482	0.473	
KF	4.042	0.041 71	0.803	0.923	0.860[b]
KCl	5.040	−0.1308	0.879	0.702	0.816[b]
KBr	5.331	0.1634	0.822	0.632	0.768[b]
KI	5.760	−0.2070	0.730	0.514	0.754[b]
RbF	4.237	−0.027 26	0.815	0.923	
RbCl	5.267	0.1090	0.927	0.702	
RbBr	5.565	−0.1396	0.883	0.632	
RbI	6.004	0.1816	0.803	0.514	
CsF	4.432	0.002 889	0.856	0.934	0.698[b]
CsCl	5.492	−0.072 90	1.000	0.734	0.744[b]
CsBr	5.805	0.1007	1.000	0.668	
CsI	6.265	−0.1409	0.949	0.555	0.761[b]
BrF	3.318	−0.2205	0.266	0.302	0.153[a]
BrCl	4.040	0.2818	0.081	0.010	0.056[a]

[a] Reference 5.

[b] Reference 6.

change parameter α_{ex}, and the corresponding wave functions for isolated atoms were used to calculate the values of $\xi_{n\lambda}$. It is easy to calculate the overlap integral $\Delta(R)$ between the wave function for CT orbitals at the interatomic distance R taken from experimental data. Numerical calculations of this integral were carried out by adopting elliptic coordinates. The calculated (q_{mol}), Pauling's (q_{Paul}), and experimental (q_{expt}) results are tabulated in Table II, along with the values of R and $\Delta(R)$. We can see that except for the molecules containing Cs atoms, the calculated results are in good agreement with the available experimental ones and that these agreements are better than in q_{Paul}. This partly verifies the validity of our assumption used for an evaluation of the Madelung constant in the case when the atoms can not be regarded as a point charge. Comparison of q_{mol} and q_{Paul} with q_{expt} for molecules containing Rb atoms would provide the more stringent test of our approach. But, unfortunately, those experimental data do not exist in the literature to our knowledge.

The extension of this assumption to crystals is very easy. For crystals with NaCl and CsCl structures whose α_M's are 1.747 56 and 1.762 67, respectively, it was found that the CT values all exactly equal 1. This is consistent with the result widely recognized.[7]

IV. CONCLUSIONS

We have derived the expression for the electron charge transfer in molecules and crystals, starting from the expansion of the total energy of an atom with respect to an occupation number. This expression takes a form similar to that of Watson *et al.*,[2] apart from the term related to the Madelung effect. By using our expression, which involves only atomic quantities for an isolated atom, the charge transfer for some diatomic molecules has been estimated. Instead of evaluating the Madelung term directly, we have made an assumption about the Madelung constant for the case when each ionized atom can not be regarded as a point charge, without a mathematical proof. Most available experimental data are well reproduced with no adjustable parameters. Applicability and limitations of our model will be clarified by many other experimental data.

APPENDIX

We shall consider the crystal given by formula $A_{ma}B_{mb}$ which consists of A atoms of N_a and B atoms of N_b. The total energy E_{cry} of this crystal is given as

$$E_{\text{cry}}=N_a\langle E\rangle_A+N_b\langle E\rangle_B+E_C+E_R\ . \qquad \text{(A1)}$$

By use of the Madelung energy ε_M given by $\alpha_M^{(\text{cry})}(m_a+m_b)\delta q_A\delta q_B/R$,[8] per a molecule composed of A atoms of m_a and B atoms of m_b, the Coulomb energy E_C is expressed as $\varepsilon_M N/(m_a+m_b)$, where $N=N_a+N_b$. Here, $\alpha_M^{(\text{cry})}$ is called a reduced Madelung constant.[8] Using the condition of charge neutrality, $x\delta q_A+y\delta q_B=0$, the total energy per an atom, f, is given as

$$f=g_{\text{cry}}+c_{\text{cry}}\ , \qquad \text{(A2a)}$$

$$g_{\text{cry}}=[\bar{\xi}_{\text{cry}}-(\alpha_M^{(\text{cry})}/R)(x/y)]q^2(R)+x\,\Delta\varepsilon\,q(R)\ , \qquad \text{(A2b)}$$

$$c_{\text{cry}}=x\langle E\rangle_A^0+y\langle E\rangle_B^0+E_R/N\ , \qquad \text{(A2c)}$$

where $\bar{\xi}_{\text{cry}}=x(\xi_{\text{CT}}^{(A)}+(x/y)\xi_{\text{CT}}^{(B)})/2$, $x\equiv N_a/N$ and $y\equiv N_b/N$. Thus, the CT value for crystals $q_{\text{cry}}(R)$ is given as

$$q_{\text{cry}}(R)=\frac{-x\Delta\varepsilon}{2[\bar{\xi}_{\text{cry}}-(\alpha_M^{(\text{cry})}/R)(x/y)]}\ . \qquad \text{(A3)}$$

We should notice that $q_{\text{mol}}(R)$ and $q_{\text{cry}}(R)$ take the same form apart from α_M, when $N_a=N_b$.

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