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Ab initio Wannier-function-based correlated calculations of Born effective charges of crystalline Li_2O and LiCl

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In this paper, we have used our recently developed *ab initio* Wannier-function-based methodology to perform extensive Hartree-Fock and correlated calculations on Li_2O and LiCl to compute their Born effective charges. Results thus obtained are in very good agreement with the experiments. In particular, for the case of Li_2O, we resolve a controversy originating in the experiment of Osaka and Shindo [Solid State Commun. **51**, 421 (1984)] who had predicted the effective charge of Li ions to be in the range of 0.58–0.61, a value much smaller compared to its nominal value of unity, thereby, suggesting that the bonding in the material could be partially covalent. We demonstrate that effective charge computed by Osaka and Shindo is the Szigeti charge, and once the Born charge is computed, it is in excellent agreement with our computed value. Mulliken population analysis of Li_2O also confirms ionic nature of the bonding in the substance.

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I. INTRODUCTION

Ab initio calculations of dielectric response properties of materials are routinely performed using methods based upon density-functional theory (DFT).[1] Most of these calculations presently are based upon the so-called "modern theory of polarization" which is based upon a Berry-phase (BP) interpretation of macroscopic polarization of solids.[2,3] The practical implementation of the BP approach within various versions of the DFT, such as the local-density approximation, is straightforward because of their mean-field nature. However, it is desirable to go beyond the mean-field level, so as to compute the influence of electron-correlation effects on polarization properties such as the Born charge of crystals. Recently, we have proposed an approach which allows computation of various polarization properties of crystalline insulators within a many-body framework.[4,5] The approach utilizes a Wannier-function-based real-space methodology, coupled with a finite-field approach, to perform correlated calculations using a Bethe-Goldstone-like many-body hierarchy. Its successful implementation was demonstrated by performing *ab initio* many-body calculations of the Born charges,[4] and optical dielectric constants,[5] of various insulating crystals. We note that an *ab initio* wave-functional-based real-space correlated approach has recently been successfully demonstrated by Hozoi *et al.*[6] to compute the quasiparticle band structure of crystalline MgO.

In this paper we apply our recently developed approach[4] to perform *ab initio* correlated calculations of the Born charges of crystalline Li_2O and LiCl. Li_2O is a technologically important material with possible applications in thermonuclear reactors,[7] as also in solid-state batteries.[8] Based upon their infrared reflectivity and Raman scattering based experiment on Li_2O, Osaka and Shindo[7] reported the value of effective charge of Li ions to be in the range of 0.58–0.61, a value much smaller compared to the nominal value of unity expected in an ionic material. Therefore, they speculated whether the nature of chemical bond in the substance is partly covalent.[7] In this work, we present a careful investigation of this subject and resolve the controversy by showing that the effective charge reported by Osaka and Shindo[7] was the Szigeti charge and not the Born charge. Once the Born charge is computed from the Szigeti charge, its experimental value of 0.95 is in excellent agreement with our theoretical value of 0.91 and much closer to the nominal value. We also present a plot of the Wannier functions in the substance as also the Mulliken population analysis to confirm the ionic bonding in Li_2O. As far as LiCl is concerned, earlier, we computed its Born charge at the Hartree-Fock level using our Wannier function methodology[9] and found its value to be significantly smaller as compared to the experiments. Therefore, in this work, we perform correlated calculations of the Born charge of LiCl and, indeed, obtain much better agreement with the experiments.

The remainder of this paper is organized as follows. In Sec. II, we briefly describe the theoretical aspects of our Wannier-function-based methodology. Next, in Sec. III, we present and discuss the results of our calculations. Finally, in Sec. IV, we present our conclusions.

II. METHODOLOGY

The Born effective charge tensor, $Z^*_{\alpha\beta}(i)$, associated with the atoms of the ith sublattice, is defined as[10]

$$Z^*_{\alpha\beta}(i) = Z_i + (\Omega/e)\frac{\partial P_\alpha^{(el)}}{\partial u_{i\beta}}\Bigg|_{\mathbf{E}=0}, \qquad (1)$$

where Z_i is the charge associated with the nuclei (or the core) of the sublattice, Ω is the volume of the unit cell, e is magnitude of the electronic charge, and $P_\alpha^{(el)}$ is the αth Cartesian component of the electronic part of the macroscopic polarization induced as a result of the displacement of the sublattice in the βth Cartesian direction, $\Delta u_{i\beta}$. For small $\Delta u_{i\beta}$, one assumes $\frac{\partial P_\alpha^{(el)}}{\partial u_{i\beta}}\big|_{\mathbf{E}=0} = \frac{\Delta P_\alpha^{(el)}}{\Delta u_{i\beta}}$, with $\Delta P_\alpha^{(el)}$ computed as the change in the electronic polarization per unit cell due to the displacement $\Delta u_{i\beta}$. For a given lattice configuration denoted by parameter λ, we demonstrated that $P_\alpha^{(el)}(\lambda)$, for a many-electron system, can be computed as the expectation value,[4]

$$P_{\alpha}^{(el)}(\lambda) = \frac{q_e}{N\Omega}\langle\Psi_0^{(\lambda)}|X_{\alpha}^{(el)}|\Psi_0^{(\lambda)}\rangle, \tag{2}$$

where, q_e $(=-e)$ is the electronic charge, N $(\rightarrow\infty)$ represents the total number of unit cells in the crystal, $X_{\alpha}^{(el)}=\Sigma_{k=1}^{N_e}x_{\alpha}^{(k)}$ is the αth component of the many-electron position operator for the N_e electrons of the crystal, and $|\Psi_0^{(\lambda)}\rangle$ represents the correlated ground-state wave function of the infinite solid, expressed in terms of the Wannier functions. For one-electron models such as Kohn-Sham theory, or the Hartree-Fock method, we showed[4] that Eq. (2) leads to expressions consistent with the Berry-phase-based theory of King-Smith and Vanderbilt[2] and Resta.[3]

Calculating the expectation value of Eq. (2) can be tedious for a general correlated wave function. We avoid this by using the finite-field approach whereby the expectation values of various components of dipole operator can be obtained by performing both the HF and correlated calculations in the presence of a small electric field in that direction and then computing the first derivative of the computed total energy with respect to the applied electric field.[4,5] This approach of computing expectation values derives its legitimacy from the generalized Hellman-Feynman theorem, and it is called "finite-field method" in quantum chemistry literature.[11] Therefore, the present set of HF and correlated calculations are distinct from our previous ones[12–16] in that the present calculations have been performed in the presence of an external electric field. For details related to our Wannier-function-based HF methodology, in the presence of external electric fields, we refer the reader to our earlier papers.[4,5]

Correlation contributions to the energy per unit cell E_{corr}, even in the presence of external electric fields, were computed according to the incremental scheme of Stoll,[17]

$$E_{corr} = \sum_i \epsilon_i + \frac{1}{2!}\sum_{i\neq j}\Delta\epsilon_{ij} + \frac{1}{3!}\sum_{i\neq j\neq k}\Delta\epsilon_{ijk} + \cdots, \tag{3}$$

where ϵ_i, $\Delta\epsilon_{ij}$, $\Delta\epsilon_{ijk}$,..., etc. are, respectively, the one-, two- and three-body,... correlation increments obtained by considering simultaneous virtual excitations from one, two, or three occupied Wannier functions, and i, j, k,... label the Wannier functions involved.[15] Because of the translational symmetry, one of these n Wannier functions is required to be in the reference unit cell, while the remaining ones can be anywhere else in the solid. In our previous studies performed on ionic systems, we demonstrated that the increments can be truncated to two-body effects ($n=2$), with the Wannier functions not being farther than the third-nearest neighbors.[15,16] We follow the same truncation scheme here as well, with the method of correlation calculation being the full-configuration interaction as in our previous works, where other technical details related to the approach are also described.[4,5,15,16]

III. RESULTS AND DISCUSSION

In this section, first we present the results of our calculations of the Born charges of Li_2O, followed by those of LiCl.

A. Li_2O

The primitive cell of Li_2O consists of a three-atom basis (two Li and one O), with each atom belonging to an fcc lattice. In our calculations, anion was placed at the origin of the primitive cell, while the cations were located at the positions $(\pm a/4 \pm a/4, \pm a/4)$. This structure is usually referred to as the antifluorite structure, to which other related materials such as Na_2O and K_2O also belong. Based upon intuition, one would conclude that the bonding in the substance will be of ionic type, with the valence $2s$ electrons of the two lithium atoms of the f.u. being transferred to the oxygen. Thus, the two Li atoms will be in cationic state, while the oxygen will be in dianionic state. However, the argument for partial covalence in the system goes as follows. It is well known that the free O^{-2} ions do not exist in nature. Therefore, in lithium oxide, it will be stabilized only because of the crystal-field effects. Still, one could argue that O^{-2} ion in solid state will be very diffuse, leading to partial covalency. In light of these arguments, it is interesting to examine the results of the experiments of Osaka and Shindo[7] performed on the single crystals of Li_2O, where they measured the frequencies of fundamental optical and Raman active modes using infrared and Raman spectroscopy. Using the measured frequencies and several other parameters, the authors fitted their data both to rigid-ion and shell models of lattice dynamics to obtain values for Li effective charges of 0.58 and 0.61,[7] respectively. Noting that the obtained effective charge is quite different from the nominal value of unity, they argued on the result which suggests that Li_2O has partially covalent character.[7] Next, we argue, however, that the effective charge reported by Osaka and Shindo is actually the Szigeti charge[18] and not the Born charge. The shell-model value of 0.61 of the effective charge of Li was computed by Osaka and Shindo[7] using the expression for the fluorite structure derived by Axe,[19]

$$Z_S = [(\nu_{LO}^2 - \nu_{TO}^2)\mu\pi r_0^3]^{1/2}\frac{3\sqrt{\epsilon_\infty}}{\epsilon_{\infty+2}}, \tag{4}$$

where ν_{LO}/ν_{TO} are the longitudinal and/or transverse optical phonon frequencies, $r_0=\frac{a}{2}$, where a is the lattice constant, μ is the effective mass of the three ion system, while ϵ_∞ is the high-frequency dielectric constant of the material. The expression in Eq. (4) is nothing but the Szigeti charge[18] of the ion from which the Born charge (Z_T) can be computed using the relation[18]

$$Z_T = \frac{(\epsilon_\infty + 2)}{3}Z_S. \tag{5}$$

If we use the values $\epsilon_\infty=2.68$ and $Z_S(\mathrm{Li})=0.61$ obtained by Osaka and Shindo[7] in Eq. (5), we obtain the experimental value of Born charge of Li ions in Li_2O to be 0.95 which is very close to the nominal value of unity. From this, the experimental value of the Born charge of the O ions can be deduced to be 1.90. These values of the Born charges of Li and O ions imply, in the most unequivocal manner, an ionic structure for Li_2O consistent with the intuition, without any possibility of covalency.

Next, we report the results of our *ab initio* correlated cal-

TABLE I. Correlated values of Born charge of Li_2O obtained in our calculations. Column with heading HF refers to results obtained at the Hartree-Fock level. Heading "one body" refers to results obtained after including the corrections due to one-body excitations from each Wannier function of the unit cell to the HF value. Two-body (O) implies results including additional corrections due to simultaneous excitations from two distinct Wannier functions located on the anion in the reference unit cell. Two-body (1NN) and two-body (2NN) correspond to two-body correlation effects involving first and second, nearest-neighbor Wannier functions, respectively.

	Oxygen Born Charge					
Basis set	HF	One body	Two Body (O)	Two body (1NN)	Two body (2NN)	Expt
(s,p)	1.794	1.783	1.763	1.781	1.777	1.90[a]
(s,p,d)	1.851	1.840	1.814	⋯	⋯	

[a] As deduced from the Szigeti charge reported in Ref. 7.

culations of Born charges of bulk Li_2O. These calculations were performed using the lobe-type Gaussian basis functions which, as demonstrated in the past, represent Cartesian Gaussian basis functions to a very good accuracy.[12–14] As in our previous HF study of the ground-state properties of Li_2O,[14] our calculations were initiated by a smaller basis set reported by Dovesi *et al.*[20] consisting of $(2s,1p)$ functions for lithium and $(4s,3p)$ functions for oxygen. However, we also augmented our basis set by a single d-type exponent of 0.8, recommended also by Dovesi *et al.*,[20] so as to check the influence of higher angular momentum functions on our results. Henceforth, we refer to these two basis sets as (s,p) and (s,p,d) basis sets, respectively. For the purpose of the calculations, fcc geometry along with the experimentally extrapolated $T=0$ lattice constant value of $a=4.573$ Å[8] was assumed. For our finite-field approach to Born charge described earlier, electric fields of strength ±0.001 a.u., along with an oxygen lattice displacement $\Delta u=0.01a$, both in the x direction, were used. This leads to the determination of Z^*_{xx} component of the Born charge corresponding to the oxygen lattice. During the correlated calculations, Wannier functions corresponding to $1s$ functions of both Li and O were held frozen, while virtual excitations were carried out from the $2s$ and $2p$ orbitals of oxygen anion. At the HF level, we verified that the symmetry relation $Z^*_{xx}=Z^*_{yy}=Z^*_{zz}$ holds, along with the fact that the off-diagonal elements of the Born charge tensor are negligible. Additionally, the optical sum rule, $Z^*_{\alpha\beta}(\mathrm{O})+2Z^*_{\alpha\beta}(\mathrm{Li})=0$, was also verified.

Our calculated results for the Born charge of oxygen in Li_2O are presented in Table I. It is obvious from the table that irrespective of the basis set used, most of the contribution to the Born charge, as expected, is obtained at the HF level, with relatively smaller contribution of electron-correlation effects. Correlation effects do diminish the value of the Born charge as compared to its HF value, however, rather insignificantly. Comparatively speaking, the inclusion of one d-type basis function on oxygen has greater influence on the Born charge of oxygen, and its value is increased as compared to the one obtained using the (s,p) basis set. With the (s,p,d) basis set, we found negligible influence on the Born charge from the two-body contributions outside of the reference unit cell. Thus, our calculations, as per optical sum rule, predict a value of Born charge of Li to be close to 0.91, in very good agreement with the experimental results,[7] with the error being less than 5%. In order to obtain a pictorial view of electronic structure in the material, in Fig. 1, we plot one of the oxygen $2p$ valence Wannier functions, computed using the (s,p,d) basis set, along the (1,1,1) direction. To simulate the effect of one of the phonon modes, we displaced the oxygen atom of the primitive cell to the position $(0.01a,0.01a,0.01a)$, where a is the lattice constant, leaving the Li atoms undisturbed. The fact that the Wannier function is highly localized around the oxygen site, with small values in the interatomic region, clearly implies the ionic character of the material.

Another quantity which could help us determine whether the system is ionic or covalent is the Mulliken population associated with the atoms of the primitive cell. With the (s,p) basis set, the Li and O Mulliken populations were found to be −2.005 and 0.984, respectively, while with the (s,p,d) basis set the populations were −2.004 and 0.984. It is obvious that the computed Mulliken populations have converged with respect to the basis set and are very close to the nominal ionicities of the two atoms. This further confirms the ionic picture of the bonding in this substance.

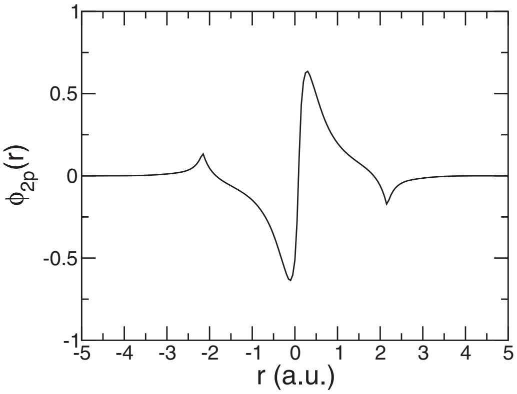

FIG. 1. One of the $2p$ valence Wannier functions of oxygen plotted along the (1,1,1) direction. In order to simulate the effect of optical phonons, calculation was performed with oxygen shifted to the position $(0.01a,0.01a,0.01a)$, and the Li positions unchanged. Nodes in the Wannier function at positions $(\pm a/4,\pm a/4,\pm a/4)$ are due to its orthogonality to the Li $1s$ Wannier functions located there.

TABLE II. Correlated values of Born charge of LiCl obtained in our calculations. Rest of the information is same as in the caption of Table I.

	Chlorine Born Charge				
Basis set	HF	One body	Two body (O)	Two body (1NN)	Expt
(s,p)	1.019	1.020	1.037	1.013	1.231[a]
(s,p,d)	1.098	1.128	1.178	⋯	

[a]Computed from the experimental data reported in Ref. 22.

B. LiCl

These calculations were performed using the basis set proposed by Prencipe *et al.*[21] in their *ab initio* HF study of alkali halides. The experimental fcc geometry with lattice constant of 5.07 Å was assumed. The unit cell employed during the calculations consisted of anion placed at the origin and the cation at the position $(a/2,0,0)$. During the many-body calculations, only the valence Wannier functions composed of $3s$, and $3p$ orbitals localized on Cl, were correlated. In order to calculate the Born charge, the anion was displaced in the x direction by an amount $0.01a$. For the finite-field computation of the dipole expectation value, an external electric field of strength ± 0.01 a.u., also along the x axis, was applied.

The results of our calculations are presented in Table II. With our (s,p) basis set, the correlation effects were included up to the level of two-body increments involving the Wannier functions in the nearest-neighboring cells. However, with the augmented (s,p,d) basis set, inclusion of two-body increments beyond the reference unit cell did not make any significant difference to the results. Similar to the case of Li_2O, we note that (a) inclusion of one d-type function improves the results both at the HF and the correlated levels and (b) the inclusion of electron-correlation effects generally improves the results as compared to the HF values. The final value of Born charge of LiCl of 1.178 obtained from these calculations is again in very good agreement with the experimental value, with an error smaller than 5%.

IV. CONCLUSIONS

In conclusion, we performed Wannier-function-based *ab initio* correlated calculations on crystalline Li_2O and LiCl to compute their Born effective charges using a methodology recently developed in our group. Calculations were performed using polarizable basis sets, and the results obtained were in very good agreement with the experimental ones. Additionally, we also resolved an ambiguity associated with rather small value of experimentally measured effective charge of Li_2O, which had raised the possibility of partial covalence in its chemical structure[7] by demonstrating that the measured charge was the Szigeti charge and not the Born charge of the compound. The Born charge obtained from the Szigeti charge was found to be in good agreement with its nominal ionic value. By further computing the Mulliken charges and exploring the Wannier functions, we demonstrated that the results were consistent with a ionic picture of Li_2O. The computational effort involved in our calculations is significantly heavier than in the calculations performed using the density-functional theory. This is because our approach is many body in nature, requiring calculations beyond the mean field. At present, we are exploring the possibility of using our approach to compute the Born charges of ferroelectric, as well as covalent materials, and we will publish our results in future as and when they become available.

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