Ab initio Hartree-Fock Born effective charges of LiH, LiF, LiCl, NaF, and NaCl

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We use the Berry-phase-based theory of macroscopic polarization of dielectric crystals formulated in terms of Wannier functions, and state-of-the-art Gaussian basis functions, to obtain benchmark *ab initio* Hartree-Fock values of the Born effective charges of ionic compounds LiH, LiF, LiCl, NaF, and NaCl. We find excellent agreement with the experimental values for all the compounds except LiCl and NaCl, for which the disagreement with the experiments is close to 10% and 16%, respectively. This may imply the importance of many-body effects in those systems.

I. INTRODUCTION

The Born effective charge (also called transverse or dynamic charge) of a crystalline system, defined as the induced polarization due to a unit sublattice displacement,[1] is a fundamental quantity connecting the electrostatic fields of the lattice to its phononic properties. It contains important information not only about the electronic structure and the bonding properties of the system, but also about the coupling of its longitudinal- and transverse-optical phonon modes to the external infrared radiation.[2–6] In addition, the Born charges also find use in first-principles-based construction of effective Hamiltonians describing phase transitions in ferroelectric materials.[7,8] Traditionally, the *ab initio* computations of Born charges of dielectrics have been performed either within the density-functional linear-response theory,[9,10] or the density-functional perturbation theory.[6,11] At a more phenomenological level, the bond-orbital method of Harrison has been very insightful.[12] Recently, however, a very elegant formalism has been proposed by King-Smith and Vanderbilt,[13] and Resta,[14,15] which formulates the general problem of symmetry-breaking-induced macroscopic polarization (of which the Born charge is a special case) of a crystalline dielectric, in terms of the Berry phase of its wave function. This Berry-phase-based approach to macroscopic polarization of dielectrics has come to be known as the ''modern theory of polarization'' (MTP) in the current physics literature.[16] The MTP has been used both within the density-functional theory (DFT) based implementations,[2,3,13,17–22] as well as the wave-function-based Hartee-Fock[23–25] (HF) formulations, to evaluate a variety of polarization-related properties.

DFT-based calculations of macroscopic polarization properties are very efficient, so that, without excessive effort, one can perform *ab initio* computations on complex compounds. Normally, the *ab initio* Born charges computed using the DFT-based formulations are within 10% agreement with the experiments for simple zinc-blende semiconductors,[5] while the disagreement can be worse for more complex systems.[16] Therefore, it is of interest to systematically explore alternative methods for computing the macroscopic polarization properties of crystalline insulators. For ionic systems, the HF method provides a powerful alternative in that it performs much better than the local-density approximation based schemes.[25,26] The other advantage of the HF method is that it can be systematically improved, both by perturbative as well as nonperturbative methods, to account for many-body effects.[27] Recently, we have developed a Wannier-function-based *ab initio* HF approach to compute the ground-state properties of crystalline insulators.[28,29] The approach has been successfully applied to compute the ground-state properties of not only three-dimensional crystals,[30–33] but also of one-dimensional periodic insulators such as polymers.[34–36] In the present paper we extend our approach to the problem of macroscopic polarization of dielectrics, and apply it to obtain benchmark HF values for the Born charges of diatomic ionic systems LiH, LiF, LiCl, NaF, and NaCl. Besides their simplicity, the main criteria behind the choice of these materials for the present paper were (a) to the best of our knowledge, no prior benchmark calculations of the Born charges of these materials exist, (b) high-quality experimental data has been available for them for a long time.[37–39] Thus by comparing the benchmark HF results such as this one, to the corresponding experimental values, one can gauge the applicability of the HF method on a wide variety of systems. When we compare the HF values of the Born charges computed in the present paper, with the experimental ones, we find that the agreement is good for LiH, LiF, and NaF, where the agreement between the theory and the experiment is always better than 7%. For NaCl and LiCl, however, the error is 10% and 16%, respectively, suggesting the possibility that the many-body effects may be stronger in these systems.

Since, this is the first application of our Wannier-function-based method to the problem of macroscopic polarization, we also present the associated computational details. The Wannier functions, being very similar in character to the molecular orbitals encountered routinely in quantum chemistry, have the added advantage of being intuitive in character. Indeed, as demonstrated later on, they lead to a pictorial description of the symmetry-breaking processes associated with macroscopic polarization of insulators.

The remainder of the paper is organized as follows. In Sec. II we briefly cover the theoretical aspects of the present paper. Our numerical results for the Born effective charges of several ionic crystals are presented in Sec. III. Finally, the conclusions are presented in Sec. IV.

II. THEORETICAL BACKGROUND

A. Born effective charge

The Born effective charge tensor $Z^*_{\alpha\beta}(i)$ associated with the atoms of the ith sublattice, is defined as[40]

$$Z^*_{\alpha\beta}(i) = Z_i + (\Omega/e) \left. \frac{\partial P^{(el)}_\alpha}{\partial u_{i\beta}} \right|_{\mathbf{E}=\mathbf{0}}, \tag{1}$$

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 the electronic charge, and $P^{(el)}_\alpha$ 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 $u_{i\beta}$. For small $\Delta u_{i\beta}$, one assumes $\partial P^{(el)}_\alpha / \partial u_{i\beta}|_{\mathbf{E}=\mathbf{0}} = \Delta P^{(el)}_\alpha / \Delta u_{i\beta}$, and computes the change in the polarization $\Delta P^{(el)}_\alpha$ following Resta's approach[14]

$$\Delta \mathbf{P}_{el} = \mathbf{P}^{(1)}_{el} - \mathbf{P}^{(0)}_{el}, \tag{2}$$

where $\mathbf{P}^{(0)}_{el}$ and $\mathbf{P}^{(1)}_{el}$, respectively, denote the electronic parts of the macroscopic polarization of the system for its initial ($\lambda=0$) and final ($\lambda=1$) states, where λ is a parameter characterizing the adiabatic symmetry-breaking transformation of the lattice. Clearly, for the present case, λ is to be identified with the sublattice displacement $\Delta u_{i\beta}$. For one-electron theories such as the Kohn-Sham theory, or the HF theory, King-Smith and Vanderbilt showed that[13]

$$\mathbf{P}^{(\lambda)}_{el} = (fe/\Omega) \sum_{n=1}^{M} \int \mathbf{r} \phi^{(\lambda)}_n(\mathbf{r})^2 d\mathbf{r}, \tag{3}$$

where $\{\phi^{(\lambda)}_n(\mathbf{r}), n=1, \ldots, M\}$ represent the M occupied Wannier functions of the unit cell for a given value of λ, and f is the occupation number of Wannier function ($f=2$, for the restricted Hartree-Fock theory). King-Smith and Vanderbilt[13] also showed that the right-hand side of Eq. (3) is proportional to the sum of the Berry phases associated with individual Wannier functions (or bands), thus equating the change in the macroscopic polarization of the solid with the change in the Berry phase of its wave function during the corresponding adiabatic transformation. In addition, Resta[15] demonstrated that $\Delta \mathbf{P}_{el}$ computed via Eqs. (2) and (3) is invariant under the choice of Wannier functions, even though the individual $\mathbf{P}^{(\lambda)}_{el}$'s are not. Computation of the Wannier functions for different values of λ is discussed in the next section.

B. Wannier functions

In principle, any approach that can yield Wannier fucntions of a crystal corresponding to its Bloch orbitals can be used to compute its Born charge tensor. However, in the present paper we have applied a framework, recently developed by us, which directly yields the restricted Hartree-Fock (RHF) Wannier functions of a crystalline insulator employing a linear combination of atomic orbitals (LCAO) approach.[28,29] In our previous work we showed that one can obtain M RHF Wannier functions, $\{|\alpha\rangle, \alpha=1, M\}$ occupied by $2M$ electrons localized in the reference unit cell $\mathcal{C}$ by solving the equations[28,29]

$$\left(T + U + \sum_\beta (2J_\beta - K_\beta) + \sum_{k \in \mathcal{N}} \sum_\gamma \lambda^k_\gamma |\gamma(\mathbf{R}_k)\rangle\langle\gamma(\mathbf{R}_k)| \right) |\alpha\rangle$$

$$= \epsilon_\alpha |\alpha\rangle, \tag{4}$$

where T represents the kinetic-energy operator, U represents the interaction of the electrons of $\mathcal{C}$ with the nuclei of the whole of the crystal, while J_β, K_β, respectively, represent the Coulomb and exchange interactions felt by the electrons occupying the βth Wannier function of $\mathcal{C}$, due to the rest of the electrons of the infinite system. The first three terms of Eq. (4) constitute the canonical Hartree-Fock operator, while the last term is a projection operator that makes the orbitals localized in $\mathcal{C}$ orthogonal to those localized in the unit cells in the immediate neighborhood of $\mathcal{C}$ by means of infinitely high-shift parameters λ^k_γ's. These neighborhood unit cells, whose origins are labeled by lattice vectors $\mathbf{R}_k$, are collectively referred to as $\mathcal{N}$. The projection operators along with the shift parameters play the role of a localizing potential in the Fock matrix, and once self-consistency has been achieved, the occupied eigenvectors of Eq. (4) are localized in $\mathcal{C}$, and are orthogonal to the orbitals of $\mathcal{N}$—thus making them Wannier functions.[28,29] As far as the orthogonality of the orbitals of $\mathcal{C}$ to those contained in unit cells beyond $\mathcal{N}$ is concerned, it should be automatic for systems with a band gap once $\mathcal{N}$ has been chosen to be large enough. As in our previous calculations performed on three-dimensional ionic insulators,[28–31] we included up to third-nearest-neighbor unit cells in the region $\mathcal{N}$.

For computing the Born charges, first $\mathbf{P}^{(0)}_{el}$ is computed from Eq. (3) using the Wannier functions of the unit cell, with all the sublattices of the crystal in their original position corresponding to the case $\lambda=0$. Next, the ith sublattice is displaced in the Cartesian direction β by a small amount $\Delta u_{i\beta}$, and $\mathbf{P}^{(1)}_{el}$ is computed in a manner identical to the previous case, except that the Wannier functions used for the purpose are recomputed for the transformed lattice. Now that we can compute $\Delta \mathbf{P}_{el}$ [cf. Eq. (2)], we can also compute the Born effective charge tensor by substituting it in Eq. (1).

The Wannier functions obtained by solving Eq. (4) are canonical Hartree-Fock solutions for the unit cell $\mathcal{C}$, and thus will satisfy the spatial symmetries of the unit cell. In appearance they look identical to the molecular orbitals encountered in any quantum-chemical calculation on a finite system, as was discussed in our earlier work.[31] Therefore, by comparing the spatial appearances of the Wannier functions for the most symmetric case ($\lambda=0$) to the broken symmetry one ($\lambda=1$), we can obtain a pictorial representation of the polarization process.

III. RESULTS AND DISCUSSION

In this section we present the results of our calculations of the Born effective charges for LiH, LiF, LiCl, NaF, and NaCl. Because of the cubic nature of the underlying Bravais lattices, the Born charge tensor for these systems has only one independent component. In all the cases, we assumed the corresponding experimental fcc crystal structure, with the anion at $(0,0,0)$ position and the cation at $(a/2,0,0)$ position, a being the lattice constant. The lattice constants used in the calculations were the theoretical ones, obtained by minimiz-

TABLE I. Born effective charges of different ionic crystals obtained in this work, as compared to the experimental values.

| Crystal | Born effective charge | | Percentage error |
	This work Z^* (theory)	Experiment Z^* (exp)	$\dfrac{[Z^*(\text{theory}) - Z^*(\text{exp})]}{Z^*(\text{exp})} \times 100$
LiH	1.046	0.991 ± 0.04 [a]	5.5
LiF	0.998	1.045[b]	-4.5
LiCl	1.036	1.231[b]	-15.6
NaF	0.956	1.024[b]	-6.6
NaCl	0.985	1.099[b]	-10.4

[a]Obtained from experimental values of the Szigeti charge Z_s, and the high-frequency dielectric constant ϵ_∞, using the relation $Z^* = [(\epsilon_\infty + 2)/3] Z_s$ (Ref. 37). Experimental Z_s and ϵ_∞ were reported in Ref. 38.

[b]Obtained from the experimental values of Z_s and ϵ_∞ reported in Ref. 39.

TABLE II. The contribution of individual Wannier functions to the Born effective charge of the alkali halides when the anion (A) sublattice with nuclear charge Z_{nuc} was translated, holding the cation (C) sublattice(s) fixed. Nominal ionicity of the anion is given in parentheses right below its Born effective charge.

| Wannier function | Nominal charge | Born effective charge | | | |
		LiF	LiCl	NaF	NaCl
$1s$ (C)	0.000	0.001	0.002	0.000	0.000
$2s$ (C)	0.000			-0.007	-0.001
$2p$ (C)	0.000			-0.216	0.002
$1s$ (A)	-2.000	-2.000	-2.000	-2.000	-2.000
$2s$ (A)	-2.000	-2.061	-2.002	-1.830	-2.001
$2p$ (A)	-6.000	-5.938	-5.998	-5.903	-5.999
$3s$ (A)	-2.000		-2.107		-2.081
$3p$ (A)	-6.000		-5.931		-5.905
Z_{nuc}		9.000	17.000	9.000	17.000
Total		-0.998	-1.036	-0.956	-0.985
		(-1.000)	(-1.000)	(-1.000)	(-1.000)

ing the total energy per unit cell at the Hartree-Fock level.

The Wannier functions used in the approach were obtained by performing all-electron HF calculations using a computer program developed by us recently.[41] In order to evaluate the centers of the Wannier functions needed for computing the polarization properties, we added a small subroutine to the existing module. The program is implemented within an LCAO approach, employing Gaussian lobe-type functions.[29] Lobe-type functions simulate the Cartesian p and higher angular momentum orbitals located on a given atomic site, as linear combinations of s-type functions slightly displaced from the site.[42] Because of this reason, it is possible that in our approach we obtain somewhat different numerical values of the Wannier function centers, as compared to the ones computed by equivalent genuine Cartesian-basis functions as implemented, e.g., in the CRYSTAL95 program.[23] For these calculations we used the lobe representation of the state-of-the-art contracted Gaussian-basis sets developed by Dovesi and co-workers.[43,44] For LiH, the details of the basis set can be obtained in Ref. 43, while for the alkali halides, they are available in Ref. 44. Using these basis sets we had studied NaCl (Ref. 30) earlier at the Hartree-Fock level; therefore, optimized lattice constants were already available for them. However, for the remaining systems, we performed fresh Hartree-Fock calculations to obtain the optimized lattice constants. The theoretical lattice constant finally used in these calculations were 4.106 Å (LiH), 4.018 Å (LiF), 4.633 Å (NaF), 5.262 Å (LiCl), and 5.785 Å (NaCl). These are in close agreement with the values 4.102 Å (LiH),[43] 4.02 Å (LiF),[44] 4.63 Å (NaF),[44] 5.28 Å (LiCl),[44] and 5.80 Å (NaCl) (Ref. 44) reported by Dovesi and co-workers.

The computed Born effective charges are presented in Table I. These results were obtained by translating the sublattices of a given crystal by the amount $\Delta u = 0.01a$ in the (100) direction. However, in order to ensure the stability of the results, several calculations were performed with different directions and magnitudes of Δu, and no significant changes in the results were observed. It was also verified by explicit calculations that the sum total of all the effective charges corresponding to the different atoms of a unit cell was always zero, in agreement with its electrical neutrality.

All these reasons give us confidence as to the correctness of our results.

From Table I it is obvious that the theoretical Born effective charges obtained for LiH and the alkali halides are quite close to their nominal ionicities. This is in perfect agreement with the intuitive picture of these systems being highly ionic in nature. As far as the comparison of the HF results with the experimental results is concerned, it is very good for LiH, LiF, and NaF. However, for NaCl and LiCl, the disagreement is more than 10%. Similar differences with respect to the experiments were also observed by Yaschenko *et al.*[24] who computed the HF Born charge of MgO to be 1.808, while the experimental value for that compound is in the range 1.96–2.02.[24] One possible reason for the discrepancy between the theoretical and the experimental values of the Born charges could be the missing many-body effects. A qualitative discussion of these many-body effects was given by Harrison, in the context of his ''ion-softening theory.''[45] When, e.g., the anionic sublattice of an alkali halide is translated, the bulk of the contribution to the Born charge—which, for the HF case, we call the mean-field contribution—is due to the electron transfer along the direction of the movement of the anion, and is associated with topmost occupied p-type Wannier function, as is obvious from Fig. 2. However, according to Harrison,[45] because of the many-body effects, we can have a single (virtual) excitation from the top p-type occupied Wannier function (the bonding orbital) into the first unoccupied Wannier function (the antibonding orbital) on the nearest-neighbor cations, thereby, modifying the Born charge. This virtual charge fluctuation, in effect, introduces some covalency into the system as compared to the mean-field HF results. In its simple parametrized form, the ion-softening theory of Harrison predicts a uniform value of $Z^* = 1.16$, for the alkali halides.[45] This value of Z^*, although reasonable, is clearly at variance with the experimental results that show a clear variation in the Z^* values of different alkali halides. Therefore, it is of interest to borrow the essence of the many-body effects incorporated in the ion-softening theory, and apply it to these
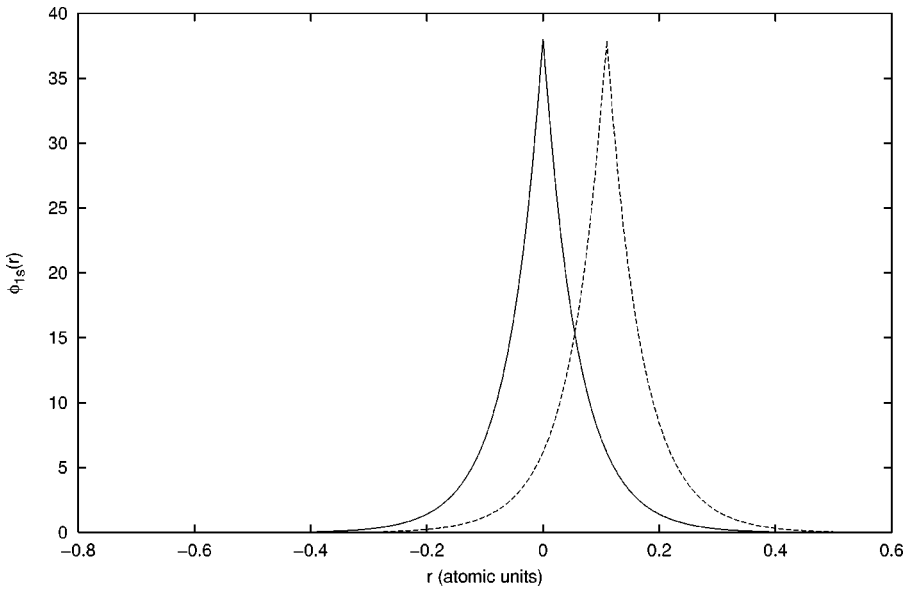
FIG. 1. Wannier functions corresponding to the $1s$ core orbital of Cl^- in NaCl for the undeformed lattice (solid line), and the deformed lattice (dashed line), plotted along the (100) direction. The deformed lattice was obtained by translating the Cl sublattice by $0.01a$ in the (100) direction. Clearly, as expected, the $1s$ Wannier function translates rigidly with the sublattice.

systems within a rigorous *ab initio* formalism, to test its applicability. Indeed, this is what we intend to explore in a future paper.

In Table II we give the detailed contributions of various Wannier functions to the Born effective charges of the alkali halides, when the anionic sublattice is translated. It is clear from the table that the low-lying corelike orbitals basically translate rigidly along with the nuclei. Nonrigid translation is seen mainly for the ns and np Wannier functions of the anion, where n defines the top of the valence band. In particular, ns orbital gains some effective charge at the expense of the n porbital. The case of NaF is an exception to this rule where the Na $2p$ Wannier function makes a significant contribution to the effective charge (-0.216). However, this contribution is due to an accidental near degeneracy of the sodium $2p$ Wannier function with the $2s$ Wannier function of fluorine, which leads to their mixture when the HF equations [cf. Eq. (4)] are solved. Because of this reason, some of the Born effective charge associated with the $2s$ Wannier function of F is transferred to the $2p$ function of Na (cf.

Table II). However, this is an instructive example of the nonuniqueness of the individual Wannier functions. But, as should be the case, the total Born charge of fluorine in NaF is free of this ambiguity associated with the individual Wannier functions, in that it has a normal value of -0.956.

It is also instructive to examine the polarization process pictorially, as depicted by Wannier functions. We shall do so for the specific case of NaCl. The $1s$ and $3p$ Wannier functions, localized on the Cl^- site of the unit cell, are plotted along the (100) direction, in Figs. 1 and 2, respectively, both before and after the translation of the Cl sublattice. As discussed earlier, on intuitive grounds we would expect the highly localized $1s$ Wannier function, which is the deepest-lying core orbital, to move rigidly with the nucleus. On the other extreme, we would expect the $3p$ Wannier function, which forms the top of the valence band, to show significant nonrigid behavior, because of its relatively delocalized character. This is indeed what we observe in Figs. 1 and 2, respectively. Owing to the perfectly cubically symmetric crystal field that the Cl site sees in the undeformed lattice, one
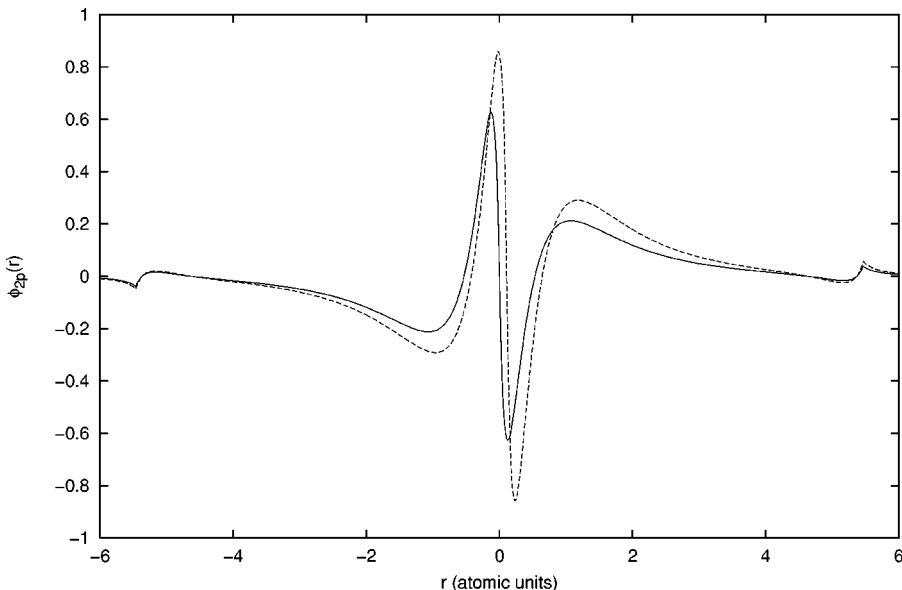

FIG. 2. Wannier functions corresponding to one of the $3p$ valence orbitals of Cl^- in NaCl before (solid line) and after (dashed line) the Cl sublattice translation. The rest of the information is the same as in the caption of Fig. 1. Unlike the core orbital, the valence Wannier function translates with significant nonrigid character, and shows signatures of broken symmetry.

would expect the corresponding $3p$ Wannier function to exhibit perfect antisymmetry about its center. Once the Cl sublattice is moved along the (100) direction, the crystal symmetry is reduced, and one would expect to see the signatures of the broken symmetry in the $3p$ Wannier function of Cl. Both these phenomena are clearly visible in Fig. 2, where, for the undeformed lattice the 3p Wannier function is perfectly antisymmetric about its center, while for the deformed case, it is no longer so, and it shows clear signs of induced polarization due to broken symmetry.

IV. CONCLUSIONS

In conclusion, we have applied the Berry-phase-based theory of macroscopic polarization, developed by King-Smith and Vanderbilt,[13] to obtain the benchmark values for the Born effective charges of several ionic compounds at the Hartree-Fock level. In the present paper, we have utilized the Wannier functions as the single-particle orbitals, and demonstrated that they lead to a pictorial description of the polarization process. As far as our results are concerned, they are in good agreement with the experiments for all the systems except LiCl and NaCl, where the disagreement with the experiments was more than 10%. One of the reasons behind this disagreement could be that the many-body effects in these systems are significant. Although there have been generalizations of the theory of macroscopic polarization to include many-body effects,[46] their implementation is not as straightforward as the single-particle theory. Recently, we have generalized our Wannier-function-based approach to include many-body effects by systematically enlarging the many-particle ground-state wave function by considering virtual excitations from the space of the occupied Wannier functions to that of the virtual ones.[33] The approach was demonstrated by computing the correlation contributions to the total energy per unit cell of bulk LiH.[33] In a future paper, we intend to generalize our approach to compute the influence of many-body effects on macroscopic polarization properties as well.

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