Ab initio Wannier-function-based many-body approach to Born charges of crystalline insulators

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In this paper we present an approach aimed at performing many-body calculations of Born-effective charges of crystalline insulators by including the electron-correlation effects. The scheme is implemented entirely in the real space, using Wannier functions as single-particle orbitals. Correlation effects are computed by including virtual excitations from the Hartree-Fock mean field, and the excitations are organized as per a Bethe–Goldstone-like many-body hierarchy. The results of our calculations suggest that the approach presented here is promising.

The Born effective charge (BEC) of a periodic solid is an important phenomenological quantity which connects the electronic structure of the system to its phononic properties.[1] Of late, in the context of ferroelectric materials and their phase transitions, BEC has generated tremendous amount of interest.[2] Using BEC, one can also describe the lattice dynamics, and its coupling to infrared radiation, in a simple intuitive manner.[3] Most of the modern calculations of BECs are based upon the Berry-phase-based theory of macroscopic polarization developed by King-Smith and Vanderbilt.[4] The aforesaid formalism is based upon single-particle orbitals, and, therefore, can be implemented in a straightforward manner within *ab initio* density-functional theory (DFT),[2,3] or the Hartree-Fock (HF) framework.[5] As far as many-body calculations of polarization properties are concerned, Martin and co-workers have proposed several approaches which, to the best of our knowledge, have not been implemented within an *ab initio* methodology.[6,7] Filippetti and Spaldin have recently implemented an *ab initio* method aimed at including correlation effects by using a self-interaction-corrected (SIC) density-functional approach.[8]

Recently, we have developed a wave-function-based *ab initio* methodology aimed at performing electronic structure calculations on crystalline insulators.[9–12] The approach uses Wannier functions as single-particle orbitals obtained at the Hartree-Fock level, which can subsequently be used to include the electron correlation effects, if needed. The approach has been applied to calculate ground state geometries, cohesive energies, and elastic properties of crystalline insulators at the Hartree-Fock level,[9,10] as well as at the correlated level.[11,12] Moreover, within the Berry-phase formalism of King-Smith and Vanderbilt,[4] we have also used our approach to compute the BECs of several ionic insulators at the HF level.[13] The purpose behind the present work is to use our Wannier-function-based methodology to perform correlated calculations of the BEC's of insulators. Since ours is a real-space approach, we start with the following expression for the electronic contribution to the polarization per unit cell ($\mathbf{P}_e$) valid for insulators:[14]

$$\mathbf{P_e}^{(\lambda)} = \frac{q_e}{N\Omega}\langle\Psi_0^{(\lambda)}|\mathbf{R}_e|\Psi_0^{(\lambda)}\rangle, \tag{1}$$

where λ is a parameter governing the state of crystal (for the present case, it represents atomic displacements), Ω is the volume of the unit cell, q_e is the electronic charge, $N(\rightarrow\infty)$, represents the total number of unit cells in the crystal, $\mathbf{R}_e = \sum_{k=1}^{N_e} \mathbf{r_k}$ is the many-particle 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. Next we verify that for an infinite crystal, Eq. (1) above is consistent with the Berry-phase-based expression for the BEC's derived by King-Smith and Vanderbilt[4] at the mean-field level. If we express the *mean field* (HF or otherwise) ground-state many-particle wave function $|\Phi_0^{(\lambda)}\rangle$ of a crystal in terms of Wannier functions expressed in terms of square-integrable occupied Wannier functions $\{W_n(\mathbf{r}-\mathbf{R_i}),\ i=1,\dots,N, n=1,\dots,M\}$ located in the N unit cells constituting the solid,[10] then using the Slater-Condon rules governing the matrix elements of a one-body operator between two many-particle states,[15] we obtain

$$\langle\Phi_0^{(\lambda)}|\mathbf{R}_e|\Phi_0^{(\lambda)}\rangle = N\sum_{n=1}^{M} f_n \int \mathbf{r}|W_n(\mathbf{r})|^2 d\mathbf{r} + n_e\left(\sum_{i=1}^{N}\mathbf{R}_i\right), \tag{2}$$

where $\{\mathbf{R_i}, i=1,\dots,N\}$ are the lattice vectors of N unit cells of the crystal, $W_n(r)$ is the nth Wannier function of the unit cell, f_n is the number of electrons in the nth Wannier function ($f_n=2$, for band insulators), M is the total number of occupied Wannier functions per unit cell, and $n_e=\sum_{n=1}^{M} f_n$ is the total number of electrons per unit cell. However, if the N unit cells are distributed among complete shells (stars), then $\sum_{i=1}^{N}\mathbf{R}_i=0$. Combining this result with Eqs. (1) and (2), we obtain the mean-field expression ($\mathbf{P}_0^{(\lambda)}$) for the polarization per cell for a crystal

$$\mathbf{P}_0^{(\lambda)} = q_e/\Omega \sum_{n=1}^{M} f_n \int \mathbf{r}|W_n^{(\lambda)}(\mathbf{r})|^2 d\mathbf{r}. \tag{3}$$

This equation is nothing but the Wannier-function version of the Berry-phase-based (mean-field) expression for macroscopic polarization derived by King-Smith and Vanderbilt,[4] who gave it an intuitive interpretation as being a sum over centers of Wannier functions of the unit cell. Note that expressions above are valid only in a real-space-based approach where square-integrable Wannier functions are used

as single-particle orbitals. If one were to use Bloch orbitals instead, the expectation value of position operator will have to be computed differently.[16] Having demonstrated the equivalence of our starting expression [Eq. (1)] to the traditional theories at the mean-field level, we next examine its implications when a many-body expression for the ground-state wave function $|\Psi_0^{(\lambda)}\rangle$, expressed in terms of virtual excitations from the mean-field wave function, is used,[15]

$$|\Psi_0^{(\lambda)}\rangle = C_{(0)}^{(\lambda)}|\Phi_0^{(\lambda)}\rangle + \sum_{n,\alpha,i,j} C_{n;\alpha}^{(\lambda)}|\Phi_0^{(\lambda)}(n \to \alpha)\rangle$$
$$+ \sum_{m,n,\alpha,\beta} C_{m,n;\alpha,\beta}^{(\lambda)}|\Phi_0^{(\lambda)}(n \to \alpha; m \to \beta)\rangle + \cdots, \quad (4)$$

where the Greek indices $\alpha, \beta, \ldots$ represent the virtual Wannier functions while the Latin indices $m, n, \ldots$ represent the occupied ones. $|\Phi_0^{(\lambda)}(n \to \alpha)\rangle$ denotes a singly excited configuration obtained by promoting one electron from the occupied Wannier function labeled n, to the virtual Wannier function labeled α. Similarly, $|\Phi_0^{(\lambda)}(n \to \alpha; m \to \beta)\rangle$ represents a doubly excited configuration with electrons being promoted from Wannier functions m, n to α, β. A noteworthy point is that the occupied $(m, n, \ldots)$ and the virtual Wannier functions $(\alpha, \beta, \ldots)$ could be located in any of the unit cells of the infinite solid. The coefficients $\{C_0^{(\lambda)}, C_{n;\alpha}^{(\lambda)}, C_{m,n;\alpha,\beta}^{(\lambda)}, \ldots\}$ can, in principle, be obtained using various available many-body techniques such as the configurations-interaction (CI) method, perturbation theory, etc. Next we examine the nature of contributions to the polarization vector $\mathbf{P}^{(\lambda)}$ arising from virtual excitations when a correlated wave function ($|\Psi_0^{(\lambda)}\rangle$) of the type of Eq. (4) is used in Eq. (1). In order to simplify things, we restrict our discussion to the contribution of the singly excited configurations $|\Phi_0^{(\lambda)}(n \to \alpha)\rangle$, although in our calculations all possible excitations needed to compute both one- and two-body increments have been considered (see the discussion below). Thus, the expectation value of the dipole operator for a singly excited many-body wave function (assuming that $|\Psi_0^{(\lambda)}\rangle$ is real) is

$$\langle\Psi_0^{(\lambda)}|\mathbf{R}_e|\Psi_0^{(\lambda)}\rangle = NC_0^{(\lambda)2}\langle\mathbf{r}\rangle_0^{(\lambda)} + 2\sqrt{2}N\sum_{n,\alpha} C_{n;\alpha}^{(\lambda)}C_0^{(\lambda)}\langle\alpha|\mathbf{r}|n(o)\rangle^{(\lambda)}$$
$$+ \cdots, \quad (5)$$

where $\langle\mathbf{r}\rangle_0^{(\lambda)} = \sum_{n=1}^{M} \int \mathbf{r}|W_n(\mathbf{r})|^2 d\mathbf{r}$ (the HF expectation value per unit cell), and, using the translational symmetry, the sum over occupied Wannier functions has been restricted to those in the reference unit cell, denoted as $|n(o)\rangle$, while the virtual Wannier function $|\alpha\rangle$ can be in any unit cell of the solid. It is clear from Eq. (5) that (a) the expectation value of the dipole operator of the entire solid $\langle\Psi_0^{(\lambda)}|\mathbf{R}_e|\Psi_0^{(\lambda)}\rangle$ scales linearly with N as it should, and (b) the correlation corrections to the dipole moment/cell such as the second term of Eq. (5), can be seen as due to the interactions between the electrons of the reference unit cell with those in the rest of the solid. Although, Eq. (5) has been derived for correlated wave functions containing only singly excited configurations, however, it is easy to verify that even for more complex wave functions, only two other types of matrix elements, viz.,

$\langle\alpha|\mathbf{r}|\beta(o)\rangle$ and $\langle m|\mathbf{r}|n(o)\rangle$ contribute to the correlated expectation value. These matrix elements originate from interaction among different types of excited configurations. Because of the localized nature of the orbitals used, the dipole matrix elements will fall to zero rapidly with the increasing distance between the orbitals involved. For example, for a typical insulating solid, the dipole matrix elements are negligible when the orbitals involved are farther than third-nearest neighbors.

Calculation of the correlated many-body wave function [Eq. (4)] of an infinite solid is an extremely difficult task, thereby rendering the direct use of Eq. (1) even more cumbersome. However, Stoll[17] proposed the use of an "incremental" method of calculating correlated total energy (and wave function) of extended systems based upon a Bethe–Goldstone-like expansion of correlation contributions. The approach was subsequently implemented by us to the case of infinite systems, and utilized to compute the total energy/cell and related quantities of bulk LiH (Ref. 11) and several polymers.[12] In the approach, the total energy/cell is written as $E_{cell} = E_{HF} + E_{corr}$, where E_{HF} is the HF energy/cell of the system, and E_{corr} is the contribution of correlation effects to the total energy/cell, computed as

$$E_{corr} = \sum_i \epsilon_i + \frac{1}{2!}\sum_{i \neq j} \Delta\epsilon_{ij} + \frac{1}{3!}\sum_{i \neq j \neq k} \Delta\epsilon_{ijk} + \cdots, \quad (6)$$

where $\epsilon_i, \Delta\epsilon_{ij}, \Delta\epsilon_{ijk}, \ldots$ 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 $i, j, k, \ldots$ label the Wannier functions involved.[11] However, using the incrementally computed many-particle wave function to compute the expectation value in Eq. (1) is a tedious task which we avoid by using generalized Hellman-Feynman theorem, and the finite-field approach to compute dipole expectation values.[15] Accordingly, we perform the incremental calculations of energy/cell with the modified Hamiltonian

$$H'(\mathcal{E}, \lambda) = H_0(\lambda) - q_e \mathcal{E} \cdot \sum_{k=1}^{N_e} \mathbf{r}_k, \quad (7)$$

where $H_0(\lambda)$ is the usual Born-Oppenheimer Hamiltonian for the solid with the given value of λ, and $\mathcal{E}$ is a user specified external electric field.[20] From $E_{cell}^{(\lambda)}(\mathcal{E})$ so computed, one can easily obtain

$$\frac{q_e\langle\Psi_0^{(\lambda)}|\mathbf{r}^j|\Psi_0^{(\lambda)}\rangle}{N} = -\frac{\partial E_{cell}^{(\lambda)}(\mathcal{E})}{\partial \mathcal{E}_j}, \quad (8)$$

where j represents the Cartesian spatial component ($j = 1, 2, 3$). The partial derivatives in Eq. (8), were computed numerically by performing the calculation of $E_{cell}^{(\lambda)}(\mathcal{E})$ for several small values of electric field $\mathcal{E}$. The Wannier functions used in the present work were obtained by solving HF equations in the presence of an electric field, and thus are different from the ones used in our earlier works.[9,10]

Next we present and discuss our results for the cases of bulk LiH and LiF. In the present study also we have used the lobe-type contracted Gaussian basis functions used in our

TABLE I. Comparison of Hartree-Fock Born charges of Li computed using the Wannier center approach [cf. Eq. (3)], and via the use of Hellman-Feynman theorem [Eq. (8)].

System	Born charge	
	Wannier-Center approach	Hellman-Feynman approach
LiH	1.0417	1.0418
LiF	0.9986	0.9983

earlier works.[9–13] Unit cell Wannier functions for both the materials were described using basis functions centered in cells as far as the third-nearest neighbors of the reference cell.[9,10] For LiH we performed the calculations using the optimized lattice constant 4.067 Å obtained in our earlier correlated calculation,[11] which is in excellent agreement with the experimental value of 4.06 Å. For LiF we used the experimental lattice constant of 3.99 Å. For both the systems, fcc geometry was assumed, and anion and cation locations in the primitive cell were taken to be $(0,0,0)$ and $(a/2,0,0)$, respectively, where a is the lattice constant. For LiH, in correlated calculations $1s$ Wannier function localized on Li as was treated as core and was held frozen, while for LiF, Wannier functions corresponding to $1s$ orbitals of both Li and F were frozen during the correlated calculations. For computing BEC's, the parameter λ corresponds to atomic displacements $\Delta\mathbf{u}$ which was taken to be $0.01a$ (a is the lattice constant) in the x direction for the anion. The BEC tensor for cubic materials is diagonal and for the ith atom of the cell it has only one unique component, say $Z^*(i)$. It was computed using the formula $Z^*(i) = Z_i + (\Omega/e)(\Delta P/\Delta u)$, where Z_i is the nuclear charge of the displaced atom, $e = |q_e|$, and ΔP is the change in the unit cell polarization due to the atomic displacement $\Delta\mathbf{u}$. For Hellman-Feynman calculations of the dipole expectation value, we used the central difference formula, with the values for the external electric field $\mathcal{E} = \pm 0.001$ a.u. in the x direction.

First we verify whether the BEC's computed using the Wannier-function centers [Eq. (3)] agree with those computed using the Hellman-Feynman theorem [Eq. (8)], at the HF level. Good agreement between the two calculations at

the HF level will be a vindication of our approach, while any serious disagreement between the two results will be a setback, and will render further correlated calculations meaningless. The results from the two calculations are presented in Table I and it is clear that the values obtained by the two methods are in excellent agreement with each other. Next we present the results of our correlated calculations in Table II. This table presents the changes in the values of BEC's as correlation effects of increasing complexity are included using the aforesaid incremental scheme. The many-body approach used to compute various correlation increments of Eq. (6) was the full-CI method, as in our earlier works.[11,12] In the case of LiH, we have performed correlated calculation including up to [third-nearest-neighbor (3NN) two-body correlation effects,[11] while for the case of LiF these calculations have been restricted to the nearest-neighbor (NN) two-body increments. The reason behind restricting the correlation effects for LiF to NN pairs is because the contributions beyond that [second-nearest-neighbor (2NN), 3NN,…] were found to be negligible. This is due to the fact that for LiH, the hydrogen anion is more diffuse as compared to the fluorine anion of LiF. Thus the valence electrons of LiH are comparatively more delocalized as compared to those of LiF, thereby making the correlation effects relatively longer range in LiH. Inspection of Table II reveals that for the case of LiH, at the HF level the BEC is overestimated, while for LiF it is underestimated. When the correlation effects within the reference unit cell are included for either of the systems, the value of the BEC decreases as compared to its HF value. This reduction can be seen as due to the mixing of the occupied Wannier function of anion with the unoccupied ones of the nearest-neighbor cation, termed "ion softening," by Harrison.[21] However, the noteworthy point is that the ion softening in the present case is being driven by the electron-correlation effects. As far as the longer-range correlation effects (1NN, 2NN,…) are concerned, no clear trends are visible in Table II. For LiH we see monotonic decrease in the value of the BEC with longer-range correlation effects, while for the case of LiF the BEC increases as the nearest-neighbor correlation effects are included. However, in both the cases, upon truncation of the correlation series, the values of the BEC's obtained are in excellent agreement with the experimental values. Finally, in order to get a feel for the magni-

TABLE II. Influence of electron correlation effects on the Born charge. Column with heading HF refers to results obtained at the Hartree-Fock level. The 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 include additional corrections due to simultaneous excitations from two distinct Wannier functions located on the anion in the reference unit cell. Two-body (NN), two-body (2NN), and two-body (3NN) correspond to two-body correlation effects involving first-, second-, and third-nearest-neighboring Wannier functions, respectively.

System	Born charge						
	HF	One-body	Two-body (O)	Two-body (NN)	Two-body (2NN)	Two-body (3NN)	Exp.
LiH	1.0418	1.0302	⋯	1.0193	1.0183	1.0003	0.991 [a]
LiF	0.9983	0.9913	0.9847	1.0237	⋯	⋯	1.045 [b]

[a]Brodsky and Burstein (Ref. 18).
[b]Computed from the experimental data reported in Ref. 19.

TABLE III. Various contributions to energy per unit cell for LiH and LiF in the absence and the presence of external electric field ($\mathcal{E}$) for the undisplaced atomic configuration ($\lambda = 0.0$). Similar calculations were also performed for distorted unit cells. For the sake of brevity we are displaying the correlation contributions only up to the NN two-body terms, but E_{cell} includes all the computed contributions.

System	$\mathcal{E}$ (a.u.)	Energy per cell (a.u.)			
		E_{HF}	$E_{corr}(O)$	$E_{corr}(NN)$	E_{cell}
LiH	0.000	−8.061 995	−0.029 551	−0.004 153	−8.096 270
	0.001	−8.065 846	−0.029 549	−0.004 153	−8.100 117
LiF	0.000	−107.045 079	−0.144 748	−0.004 434	−107.194 261
	0.001	−107.048 856	−0.144 744	−0.004 430	−107.198 030

tude of correlation effects with and without the electric field, we present the values of various contributions to the correlation energy/cell for the two systems in Table III computed for the undistorted unit cell ($\lambda = 0$). Results of similar calculations performed for the distorted unit cell are not presented here for the sake of brevity. From the table it is obvious that, as expected, the most important corrections to E_{cell}, due to the electric field, are at the HF level. The correlation energies in the nonzero field are reduced by small amounts as compared to their zero-field counterparts. Of course, these small changes in correlation energies for the $\lambda = 0$ and $\lambda \neq 0$ case in the end lead to the correlation corrections to the BEC's as depicted in Table II.

In conclusion, we have presented an *ab initio* Wannier-function-based many-body approach aimed at computing the Born effective charges of insulators. However, it is clear from the approach that it can also be used to compute other properties such as high-frequency dielectric constant, piezoelectric tensor, etc. of insulators. Work along these lines is presently under way in our group, and the results will be presented in future publications.

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