Electronic polarization in the ultrasoft pseudopotential formalism

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Abstract

An expression is given for the electronic polarization of an insulating crystal within the ultrasoft pseudopotential scheme. The pseudopotential charge-augmentation terms modify the usual Berry-phase expression, and also give rise to a second term that takes the form of a conventional expectation value.

Several years ago, we presented a formulation that allows for the calculation of the electronic polarization of an insulating crystal in the context of a conventional electronic band-structure calculation.[1,2] It was shown that the contribution of a given band to the electronic polarization could be expressed in terms of the charge center of its associated Wannier function; or equivalently, in terms of the Berry phase of the cell-periodic Bloch function $u_{\mathbf{k}}$ as the wavevector $\mathbf{k}$ is adiabatically transported by a reciprocal lattice vector. Resta has given a review of this theory.[3]

The above theory can be applied straightforwardly in the context of an all-electron (e.g, augmented plane-wave) scheme, or any norm-conserving pseudopotential scheme. However, in the ultrasoft pseudopotential scheme,[4–6] the pseudo-wavefunctions do not obey a conventional normalization condition, and the Berry-phase expression must be modified.

The purpose of this Report is to present the appropriate formulation of the electronic polarization within the ultrasoft pseudopotential scheme. The expression has already been used in applications,[7,8] but has never previously been reported.

Let $l = \{\mathbf{R}, \tau\}$ label the atomic sites in the crystal, where $\mathbf{R}$ is a real-space lattice vector and τ is the extra fractional translation needed to specify the location of the atom in the cell. Note that τ will double as a species label for the atom. The basic ingredients of the USPP scheme[4–6] are the projectors $\beta_{\tau,i}(\mathbf{r})$ and the charge augmentation functions $Q_{\tau,ij}(\mathbf{r})$ for an atom of species τ. Here i is a composite index labeling the angular momentum (lm) and radial indices of the projectors. The matrix quantities $Q_{\tau,ij}$ and $\mathbf{d}_{\tau,ij}$ are then defined via

$$Q_{\tau,ij} = \int d\mathbf{r}\, Q_{\tau,ij}(\mathbf{r}) \tag{1}$$

and

$$\mathbf{d}_{\tau,ij} = \int d\mathbf{r}\, \mathbf{r}\, Q_{\tau,ij}(\mathbf{r}) \quad . \tag{2}$$

The projectors and charge augmentation functions of atom l located in the crystal at $\mathbf{R} + \tau$ are

$$\beta_i^{(l)}(\mathbf{r}) = \beta_{\tau,i}(\mathbf{r} - \mathbf{R} - \tau) \tag{3}$$

and

$$Q_{ij}^{(l)}(\mathbf{r}) = Q_{\tau,ij}(\mathbf{r} - \mathbf{R} - \tau) \quad . \tag{4}$$

The charge density operator in the crystal is thus[5]

$$K(\mathbf{r}) = |\mathbf{r}\rangle\langle\mathbf{r}| + \sum_l \sum_{ij} Q_{ij}^{(l)}(\mathbf{r})\, |\beta_i^{(l)}\rangle\, \langle\beta_j^{(l)}| \tag{5}$$

and the number operator is $S = \int d\mathbf{r}\, K(\mathbf{r})$ or

$$S = 1 + \sum_l \sum_{ij} Q_{\tau,ij}\, |\beta_i^{(l)}\rangle\, \langle\beta_j^{(l)}| \quad . \tag{6}$$

The Bloch pseudo-wavefunctions $\psi_{\mathbf{k}}$ are written in terms of cell-periodic functions $u_{\mathbf{k}}$ in the usual way,

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\, u_{\mathbf{k}}(\mathbf{r}) \quad . \tag{7}$$

The normalization $\langle\psi_{\mathbf{k}}|S|\psi_{\mathbf{k}}\rangle_V = 1$ is relative to the number operator of Eq. (6). (The notation $\langle\rangle_V$ indicates that the expectation value or matrix element is taken per unit cell of volume V.) Substituting Eq. (6) and using the definition

$$\beta^{(\mathbf{k})}_{\tau,i}(\mathbf{r}) = e^{-i\mathbf{k}\cdot(\mathbf{r}-\tau)}\, \beta_{\tau,i}(\mathbf{r}-\tau) \quad , \tag{8}$$

the normalization of the cell-periodic Bloch function becomes

$$1 = \langle u_{\mathbf{k}}|u_{\mathbf{k}}\rangle_V + \sum_\tau \sum_{ij} Q_{\tau,ij}\, \langle u_{\mathbf{k}}|\beta^{(\mathbf{k})}_{\tau,i}\rangle\, \langle\beta^{(\mathbf{k})}_{\tau,j}|u_{\mathbf{k}}\rangle \quad . \tag{9}$$

Now, from the Bloch pseudo-wavefunctions, one can construct a localized Wannier pseudo-wavefunction in the usual way,

$$|w\rangle = \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k}\, |\psi_{\mathbf{k}}\rangle \quad , \tag{10}$$

where the integral is over the Brillouin zone (BZ). It is straightforward to check the normalization $\langle w|S|w\rangle = 1$, viz.,

$$\begin{aligned}
\langle w|S|w\rangle &= \langle w|w\rangle + \sum_l \sum_{ij} Q_{\tau,ij}\, \langle w|\beta^{(l)}_i\rangle\, \langle\beta^{(l)}_j|w\rangle \\
&= \frac{V^2}{(2\pi)^6}\int_{\mathrm{BZ}} d\mathbf{k} \int_{\mathrm{BZ}} d\mathbf{k}' \sum_{\mathbf{R}} \Big\{ \int_V d\mathbf{r}\, u^*_{\mathbf{k}}(\mathbf{r})\, u_{\mathbf{k}'}(\mathbf{r})\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}+\mathbf{r})} \\
&\qquad + \sum_\tau \sum_{ij} Q_{\tau,ij}\, \langle u_{\mathbf{k}}|\beta^{(\mathbf{k})}_{\tau,i}\rangle\, \langle\beta^{(\mathbf{k}')}_{\tau,j}|u_{\mathbf{k}'}\rangle\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}+\tau)} \Big\} \\
&= \frac{V}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{k} \Big\{ \langle u_{\mathbf{k}}|u_{\mathbf{k}}\rangle_V + \sum_\tau \sum_{ij} Q_{\tau,ij}\, \langle u_{\mathbf{k}}|\beta^{(\mathbf{k})}_{\tau,i}\rangle\, \langle\beta^{(\mathbf{k})}_{\tau,j}|u_{\mathbf{k}}\rangle \Big\} \quad .
\end{aligned} \tag{11}$$

The second line results from substituting Eqs. (6) and (10), and the third is obtained from the completeness relation

$$\sum_{\mathbf{R}} e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = \frac{(2\pi)^3}{V}\, \delta(\mathbf{k}-\mathbf{k}') \quad . \tag{12}$$

Using the Bloch normalization of Eq. (9), it then follows that $\langle w|S|w\rangle = 1$.

The contribution of this band to the electronic polarization is given in terms of the Wannier center as $(-2e/V)\langle\mathbf{r}\rangle$, assuming spin-paired electrons.[1–3] Thus, our remaining task is to calculate the location $\langle\mathbf{r}\rangle$ of the Wannier center. Using Eqs. (1), (2), (4), and (5),

$$\begin{aligned}
\langle\mathbf{r}\rangle &= \int d\mathbf{r}\, \mathbf{r}\, \langle w|K(\mathbf{r})|w\rangle \\
&= \langle w|\mathbf{r}|w\rangle + \sum_l \sum_{ij} \Big[(\mathbf{R}+\tau)Q_{\tau,ij} + \mathbf{d}_{\tau,ij}\Big]\, \langle w|\beta^{(l)}_i\rangle\, \langle\beta^{(l)}_j|w\rangle \quad .
\end{aligned} \tag{13}$$

Substituting Eq. (10), one obtains, in analogy with the second line of Eq. (11),

$$\langle \mathbf{r} \rangle = \frac{V^2}{(2\pi)^6} \int_{\rm BZ} d\mathbf{k} \int_{\rm BZ} d\mathbf{k}' \sum_{\mathbf{R}} \Bigg\{ \int_V d\mathbf{r}\, u^*_{\mathbf{k}}(\mathbf{r})\, (\mathbf{R}+\mathbf{r})\, u_{\mathbf{k}'}(\mathbf{r})\, e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}+\mathbf{r})}$$

$$+ \sum_\tau \sum_{ij} [(\mathbf{R}+\tau) Q_{\tau,ij} + \mathbf{d}_{\tau,ij}]\, \langle u_{\mathbf{k}} | \beta^{(\mathbf{k})}_{\tau,i} \rangle \, \langle \beta^{(\mathbf{k}')}_{\tau,j} | u_{\mathbf{k}'} \rangle \, e^{-i(\mathbf{k}-\mathbf{k}')\cdot(\mathbf{R}+\tau)} \Bigg\} \ . \tag{14}$$

Replacing $\mathbf{R}+\mathbf{r}$ or $\mathbf{R}+\tau$ by $-i\nabla_{\mathbf{k}'}$ acting on the exponential factor, then using an integration by parts to cause $\nabla_{\mathbf{k}'}$ to act on the $u_{\mathbf{k}'}$ and $\beta^{(\mathbf{k}')}$ instead, and applying the completeness relation (12), one finds

$$\langle \mathbf{r} \rangle = \langle \mathbf{r} \rangle^{\rm BP} + \langle \mathbf{r} \rangle^{\rm EV} \tag{15}$$

where

$$\langle \mathbf{r} \rangle^{\rm BP} = \frac{V}{(2\pi)^3} \int_{\rm BZ} d\mathbf{k}\, \mathbf{A}(\mathbf{k}) \ , \tag{16}$$

$$\langle \mathbf{r} \rangle^{\rm EV} = \frac{V}{(2\pi)^3} \int_{\rm BZ} d\mathbf{k} \sum_\tau \sum_{ij} \mathbf{d}_{\tau,ij}\, \langle u_{\mathbf{k}} | \beta^{(\mathbf{k})}_{\tau,i} \rangle \, \langle \beta^{(\mathbf{k})}_{\tau,j} | u_{\mathbf{k}} \rangle \ , \tag{17}$$

and

$$\mathbf{A}(\mathbf{k}) = i\, \langle u_{\mathbf{k}} | \nabla_{\mathbf{k}} | u_{\mathbf{k}} \rangle_V + \sum_\tau \sum_{ij} i\, Q_{\tau,ij}\, \langle u_{\mathbf{k}} | \beta^{(\mathbf{k})}_{\tau,i} \rangle \, \nabla_{\mathbf{k}} \, \langle \beta^{(\mathbf{k})}_{\tau,j} | u_{\mathbf{k}} \rangle \ . \tag{18}$$

The decomposition (15) is into "Berry-phase" (BP) and "expectation-value" (EV) terms. The latter involves no coupling between k-points [cf. Eq. (17)] and is thus obviously gauge-invariant, i.e., invariant with respect to a k-dependent change of phase of the $u_{\mathbf{k}}$. The BP term is also gauge-invariant, as can be seen by substituting $u_{\mathbf{k}} \rightarrow u_{\mathbf{k}} \times \exp[-i\gamma(\mathbf{k})]$ into (18) and using the Bloch normalization condition (9) to show that $\mathbf{A}(\mathbf{k}) \rightarrow \mathbf{A}(\mathbf{k}) + \nabla_{\mathbf{k}}\gamma(\mathbf{k})$. The quantity $\mathbf{A}(\mathbf{k})$ thus plays the role of the "Berry connection" or "gauge potential" of the Berry-phase theory.[9,10] Since $\exp[-i\gamma(\mathbf{k})]$ is periodic in k-space, it follows that $\gamma(\mathbf{k})$ must take the form of $\mathbf{R}\cdot\mathbf{k}$ plus a periodic part ($\mathbf{R}$ being a lattice vector), so that $\langle \mathbf{r} \rangle^{\rm BP}$ is clearly invariant modulo a lattice vector.

In practical calculations, a discrete mesh of k-points is typically used. The expectation-value term is easily evaluated on any mesh of N_k k-points as

$$\langle \mathbf{r} \rangle^{\rm EV} = \frac{1}{N_k} \sum_{\mathbf{k}} \sum_\tau \sum_{ij} \mathbf{d}_{\tau,ij}\, \langle u_{\mathbf{k}} | \beta^{(\mathbf{k})}_{\tau,i} \rangle \, \langle \beta^{(\mathbf{k})}_{\tau,j} | u_{\mathbf{k}} \rangle \ . \tag{19}$$

Following Ref. 1, the Berry-phase term is evaluated one component at a time. That is, the component of $\langle \mathbf{r} \rangle^{\rm BP}$ along some primitive reciprocal lattice vector $\mathbf{G}$ is evaluated by choosing a 2D mesh of $N_{k\perp}$ strings of k-points running parallel to $\mathbf{G}$, and calculating

$$\langle r_{\|} \rangle^{\rm BP} = \frac{-1}{G N_{k\perp}} \sum_{\mathbf{k}_\perp} {\rm Im}\ \ln \prod_{k_\|} \left\{ \langle u_{\mathbf{k}} | u_{\mathbf{k}+\mathbf{b}} \rangle_V + \sum_\tau \sum_{ij} Q_{\tau,ij}\, \langle u_{\mathbf{k}} | \beta^{(\mathbf{k})}_{\tau,i} \rangle \, \langle \beta^{(\mathbf{k}+\mathbf{b})}_{\tau,j} | u_{\mathbf{k}+\mathbf{b}} \rangle \right\} \ . \tag{20}$$

Here $r_{||}$ and $k_{||}$ are components of $\mathbf{r}$ and $\mathbf{k}$ parallel to $\mathbf{G}$, with $\mathbf{k} = \mathbf{k}_\perp + k_{||}\hat{\mathbf{G}}$, and $\mathbf{b}$ being the separation between neighboring k-points along the strings. As in Ref. 1, this discrete version of the Berry-phase term is manifestly invariant with respect to a change of phase of any one of the $u_{\mathbf{k}}$, since each $u_{\mathbf{k}}$ appears once in a bra and once in a ket.

For the case of multiple discrete bands, the final expression for the polarization is

$$\mathbf{P} = \mathbf{P}_{\mathrm{ion}} - \frac{2e}{V} \sum_n \left[\langle \mathbf{r} \rangle_n^{\mathrm{BP}} + \langle \mathbf{r} \rangle_n^{\mathrm{EV}} \right] \;, \tag{21}$$

where the sum is over occupied bands n. For the case of compound multiple bands that have degeneracies at certain locations within the Brillouin zone, the EV terms present no difficulties, but the BP evaluation requires care. One can again follow the example of Ref. 1 to express the Berry-phase contribution to the electronic polarization as

$$\mathbf{P}^{\mathrm{BP}} = \frac{-2e}{V} \frac{1}{G N_{k\perp}} \sum_{\mathbf{k}_\perp} \mathrm{Im} \ln \prod_{k_{||}} \det M^{(\mathbf{k})} \tag{22}$$

where

$$M_{mn}^{(\mathbf{k})} = \langle u_{m,\mathbf{k}} | u_{n,\mathbf{k}+\mathbf{b}} \rangle_V + \sum_\tau \sum_{ij} Q_{\tau,ij} \, \langle u_{m\mathbf{k}} | \beta_{\tau,i}^{(\mathbf{k})} \rangle \, \langle \beta_{\tau,j}^{(\mathbf{k}+\mathbf{b})} | u_{n,\mathbf{k}+\mathbf{b}} \rangle \tag{23}$$

and the indices m and n run over occupied bands.

In summary, the formulas for electronic polarization given in Ref. 1 have been generalized to the case in which ultrasoft pseudopotentials have been used in the band-structure calculation. The resulting formulas are easily implemented in practice.

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