Theory of polar corrections to donor binding

G. D. Mahan and Kristian Berland

1Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802, USA
2Department of Microtechnology and Nanoscience, Chalmers Technical University, Göteborg, Sweden

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We present calculations of donor binding energies for cubic materials. Previous theories calculated the Rydberg energy reduced by the effective mass and the static dielectric function. They omitted an important energy term from the long-range polarization of the ionized donor, which vanishes for the neutral donor. They also omitted the donor-phonon interaction. The inclusion of these terms yields a new formula for the donor binding energy.

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I. INTRODUCTION

We present a calculation of the polaron correction to the binding energy $E_D$ of electrons to donors. This topic was treated originally by Larsen.1–6 We adopt a similar approach, but include more terms in the theory.

Prior theories are called the scaled hydrogen model (SHM). In the SHM, one takes the binding energy of hydrogen, i.e., the Rydberg energy, and scales it with the effective band mass $m^*$ of the electron, and the dielectric function $\varepsilon$ of the material. In SI units,

$$E_D = \frac{e^4 m^*}{2(4\pi \varepsilon)\hbar^2}. \quad (1)$$

For weakly bound donors, the dielectric function is usually taken to be the zero-frequency value $\varepsilon(0)$, which includes the polar contribution from optical phonons. When the donor binding energy is larger than the optical-phonon energy, some researchers advocate using the high-frequency dielectric constant $\varepsilon(\infty)$. Neither our theory nor that of Larsen is able to derive these expressions for the SHM. We show below that our theory gives the formula for the effective dielectric constant,

$$\frac{1}{\varepsilon} = \frac{5}{16\varepsilon(\infty)} + \frac{11}{16\varepsilon(0)}. \quad (2)$$

The fractional factors are unexpected and are the main result of our calculation. The SHM is still in regular use today.7–10

In doing this calculation, we became aware that prior theories omitted an important energy term: the polarization energy of the ionized donor. An ionized donor is viewed as a point charge in a polarizable medium. There is a polarization energy associated with this long-range potential. We calculate below the exact expression for this energy. When the electron becomes bound to the donor, the donor becomes neutral, and the long-range polarization energy vanishes. It is replaced by short-range polarization on the scale of the Bohr radius of the donor. This difference in polarization energy contributes to the binding energy of the donor. It is one reason for the fractions in Eq. (2).

We present calculations of donor binding energies for materials with the fcc (face-centered-cubic) lattice. This includes most III-V and II-VI semiconductors, and some oxides. For semiconductors with small donor binding energies, we get similar accuracy compared to the SHM. For the oxides, in particular, our theory gives much larger binding energies than does the SHM, but neither agree with experiment. Our theory may also apply to the binding of holes to acceptors. However, the degeneracy of most valence bands makes this case more complicated, and we do not consider the acceptor case.

Landau and Pekar11–13 developed the first theory of polarons for a free electron. They did a variational calculation on an electron eigenfunction, $\phi(r)$. They calculated the phonon displacement $\delta Q$ in response to the charge density of this eigenfunction, and then calculated the polaron energy $\propto (\delta Q)^2$. This phonon excess energy then became part of the variational energy determining the electron eigenfunction. The Landau-Pekar theory later became recognized as the strong-coupling theory of polarons.14 Here we adopt the same procedure to calculate the response of the phonons to the electron bound to the donor. Instead of the Gaussian eigenfunction used by Landau and Pekar, we use the exponential eigenfunction typical of a donor. Otherwise our calculation follows the same procedures. Obviously, our theory is also a strong-coupling theory, which applies when $\varepsilon(\infty)$ and $\varepsilon(0)$ are very different.

II. THEORY

We employ an approach based on our earlier work.15,16 The Hamiltonian includes optical phonons, donors at $R_i$ of charge $q > 0$, and an electron of charge $e < 0$, with effective mass $m^*$, which may be bound to a donor. The optical phonons have a displacement $Q_j$, with a Szigeti charge $e^*$, which creates a dipole $e^*Q_j$.

$$H = \frac{p_j^2}{2m} + \sum_i \frac{eq}{4\pi \varepsilon(\infty)|r - R_i|} + \frac{q^2}{4\pi \varepsilon(\infty)} \sum_{l>j} \frac{1}{|R_l - R_i|}$$

$$+ \sum_j \left[ \frac{p_j^2}{2M} + \frac{K}{2} Q_j^2 \right] + V_{pd} + V_{ep} + V_{pp}, \quad (3)$$

where

(i) the interaction between the phonons and the donors is

$$V_{pd} = -\frac{e^*q}{4\pi \varepsilon(\infty)} \sum_{j,l} \frac{Q_j \cdot (R_j - R_l)}{|R_j - R_l|^3}. \quad (4)$$
The second term in $KL$ coordinates, an electron nearby. We transform the vibrations to collective G. D. MAHAN AND KRISTIAN BERLAND PHYSICAL REVIEW B

\[ V_{pp} = -\frac{(e^*)^2}{8\pi \varepsilon(\infty)} \sum_{i,j} Q_i \cdot \phi_{ij} \cdot Q_j, \]

where $n(r)$ is the charge density of an electron bound to the donor, and which reduces to the usual Fröhlich interaction for electrons in a free-energy band,17 and

(iii) the dipole-dipole interaction between the phonons is

\[ V_{pd} = -\frac{q e^*}{4\pi \varepsilon(\infty) \sqrt{N}} \sum_k Q_k \cdot W_k \sum_l e^{i k \cdot R_l}, \]

\[ W_k = \sum_{j \neq 0} e^{i k \cdot R_j} R_j \approx \frac{4\pi i k}{\Omega_0 k^2}, \]

where the latter limit is for long wavelength. In this case, the expression for $\beta_k$ is

\[ \beta_k = -\frac{q e^* i}{\varepsilon(\infty) k \Omega_0 \sqrt{N}} \sum_l e^{i k \cdot R_l}. \]

The phonon displacements enter as $(k \cdot Q_k)$, where the notation emphasizes that only longitudinal-optical phonons are involved. The transverse- ($\omega_{TO}$) and longitudinal- ($\omega_{LO}$) optical-phonon frequencies are defined as

\[ \omega_{TO}^2 = K \frac{K_{LO}^2}{M} = K \frac{1}{3} \omega_0^2, \]

\[ \omega_{LO}^2 = K \frac{K_{LO}^2}{M} + \frac{2}{3} \omega_0^2, \]

\[ \omega_0^2 = \left( \frac{e^*}{M \Omega_0 \varepsilon(\infty)} \right)^2. \]

The static dielectric function is

\[ \varepsilon(0) = \varepsilon(\infty) \left[ 1 + \frac{\omega_0^2}{\omega_{TO}^2} \right]. \]

We complete the square on the interaction in Eq. (11),

\[ V = \frac{K}{2k} \sum_k \left[ k \cdot Q_k + \frac{\beta_k}{K_{KL}} \right]^2 - \frac{1}{2K_L} \sum_k |\beta_k|^2. \]
IV. ELECTRON BOUND TO DONOR

We repeat the above calculation but include an electron bound to a donor at $\mathbf{R}_i$. We do this calculation of the donor binding energy using a variational parameter $\alpha$ defined as

$$\psi(r) = \sqrt{\frac{\alpha^3}{\pi a_0^6}} \exp[-\alpha r/a_0], \quad (28)$$

$$n(r) = |\psi(r)|^2, \quad (29)$$

where the Bohr radius is given by

$$a_0 = 4\pi \varepsilon(\infty) \frac{\hbar^2}{e^2m^*}, \quad (30)$$

and $m^*$ is the band effective mass of the conduction electron. Larsen\textsuperscript{1} did a similar calculation but omitted the interaction $V_{pd}$, which is the term that polarizes the lattice in the absence of an electron. The inclusion of this important term is crucial for including all essential interactions. Again, we transform the vibrations to collective coordinates,

$$Q_j = \frac{1}{\sqrt{N}} \sum_k e^{i\mathbf{R}_k \cdot \mathbf{Q}_j}. \quad (31)$$

The potential-energy terms in the limit of long wavelength are

$$V = -\sum_k \left[ \frac{K_L}{2} (\mathbf{k} \cdot \mathbf{Q}_j)^2 + \gamma_k \mathbf{k} \cdot \mathbf{Q}_k \right], \quad (32)$$

$$\gamma_k = \frac{i e^*}{\varepsilon(\infty) k a_0 \sqrt{N}} \left[ q + e\Lambda(k a_0/2\alpha) \right] \sum_i e^{i\mathbf{k} \cdot \mathbf{R}_j}, \quad (33)$$

$$\Lambda(x) = \frac{1}{(1 + x^2)^2}. \quad (34)$$

The first term in $\gamma_k$ comes from the donor-phonon interaction, and the second term comes from the electron-phonon interaction. The donor-phonon interaction is evaluated in the long-wavelength limit. We complete the square on the interaction, and also set $q = -e$,

$$V = \frac{K_L}{2} \sum_k \left[ \mathbf{k} \cdot \mathbf{Q}_k + \frac{\gamma_k}{K_L} \right]^2 - \frac{1}{2K_L} \sum_k |\gamma_k|^2. \quad (35)$$

The last term is part of the effective interaction between the electron and the donor due to the phonon polarization,

$$V'' = -\frac{1}{2K_L} \sum_k |\gamma_k|^2. \quad (36)$$

$$V'' = -\frac{e^2(\varepsilon(\infty))^2}{2K_L \varepsilon(\infty)^2 \Omega_L} \int \frac{d^3k}{(2\pi)^3} \frac{1}{k^2}$$

$$\times \left[ 1 - \Lambda(k a_0/2\alpha) \right]^2 \sum_i e^{i\mathbf{k} \cdot \mathbf{R}_i - i\mathbf{k} \cdot \mathbf{R}_j}. \quad (37)$$

We evaluate this expression below in several limits. There are two types of terms. If $l \neq l'$, then it is the phonon-induced interaction between two neutral donors. If $l = l'$, then it is the polaron correction to the binding energy of a single donor. Note that $\Lambda(x = 0) = 1$ so the integrand vanishes at $k = 0$. There is no long-range Coulomb interaction between neutral donors.

A. Interactions between donors

First, consider the case of $l \neq l'$ so the expression gives the phonon-induced interaction energy between two neutral donors. For the effective mass limit, where the orbit radius $a_0$ covers many lattice constants, we can extend the limit of integration to infinity. We change to dimensionless variables $x = k a_0/(2\alpha)$, $y = 2\alpha R_{ll'}/a_0$, and we get

$$V'' = -\frac{e^2}{4\pi \varepsilon(\infty) a_0} \frac{\omega_L^2}{\Omega_L} I(y), \quad (38)$$

$$I(y) = \frac{2}{\pi y} \int_0^\infty dx \sin(xy) \frac{x^3(2 + x^2)^2}{(1 + x^2)^3}. \quad (39)$$

The above integral can be evaluated by contour integration. It gives the term

$$I(y) = \frac{e^{-y} y^3}{y} \sum_{m=0}^{11} a_m y^m. \quad (40)$$

The interaction decays exponentially, which is typical of the interaction between neutral-charge distributions when neglecting correlations.

B. Neutral donor number 1

We evaluate Eq. (37) for the case of $l = l'$. We expand the factor as

$$(1 - \Lambda)^2 = 1 - 2\Lambda + \Lambda^2. \quad (41)$$

We evaluate the first term (“1”) as Eq. (27), so the polarization energy of the donor is unchanged. The other two terms contribute to the donor binding energy. In the effective mass limit, the last two terms are evaluated assuming that the $k$ integral goes to infinity,

$$\frac{4\pi}{(2\pi)^3} \int_0^\infty dk [-2\Lambda + \Lambda^2] = -\frac{\alpha}{2\pi a_0} \left[ 1 - \frac{5}{16} \right] = -\frac{11\alpha}{32\pi a_0}. \quad (42)$$

The variational energy for the donor binding is

$$\mathcal{E}(\alpha) = E_R_1 [\alpha^2 - 2\alpha(1 - \lambda)], \quad \lambda = \frac{11}{16} \frac{\omega_L^2}{\omega_L^2}. \quad (43)$$

Minimizing with respect to $\alpha$ gives

$$\alpha_0 = 1 - \lambda = \frac{5}{16} + \frac{11 \varepsilon(\infty)}{16 \varepsilon(0)}. \quad (44)$$

$$\mathcal{E}(\alpha_0) = -E_R_1 (1 - \lambda)^2. \quad (45)$$

For weakly bound donors, the dielectric screening is not given by either $\varepsilon(\infty)$ or $\varepsilon(0)$. Instead, it is $5/16$ of $\varepsilon(\infty)$ and $11/16$ of $\varepsilon(0)$.

An interesting result is obtained if we neglect $\Lambda^2$. In that case, the total variational energy for the electron bound to the donor is

$$\mathcal{E}(\alpha) = \frac{\hbar^2 \alpha^2}{2m^*a_0^2} - \frac{e^2\alpha}{4\pi \varepsilon(\infty) a_0} \left( 1 - \frac{11\alpha^2}{\omega_L^2} \right). \quad (46)$$

$$\mathcal{E}(\alpha) = \frac{\hbar^2 \alpha^2}{2m^*a_0^2} - \frac{e^2\alpha}{4\pi \varepsilon(0) a_0}. \quad (47)$$
Varying \( a \) gives the minimum,

\[
\alpha_0 = \left[ \frac{\varepsilon(\infty)}{\varepsilon(0)} \right].
\]  

The donor binding energy is screened by the zero-frequency dielectric function, which includes the contribution from the optical phonons. This is the usual form of the SHM, which is obtained only by neglecting \( \Delta^2 \). Since neglecting \( \Delta^2 \) is a poor approximation, the SHM is not accurate.

C. Neutral donor number 2

Here we evaluate the screening corrections to the neutral donor by a different method, which calculates all energy terms in real space. This has the advantage of not having to make a long-wavelength approximation. The final expression should be more accurate.

The interaction \( V_{ep} \) is rewritten as

\[
V_{ep} = \frac{ee^*}{4\pi \varepsilon(\infty)\sqrt{N}} \sum_k \left( \sum_l e^{ikR_l} \right) \times \sum_{j\neq0} e^{ikR_j} Q_k \cdot \vec{\nabla}_{R_j} f(R_j),
\]  

\[
f(R) = \int d^3r \frac{n(r)}{|R - r|} = \frac{1}{R} - \frac{1}{R} e^{-2\alpha R/a_0} \left( 1 + \frac{\alpha R}{a_0} \right).
\]  

When \( q = -e \), the \( 1/R \) term cancels \( V_{pd} \). The combined terms give, for \( \gamma_k \)

\[
\gamma_k = -\frac{ee^*}{4\pi \varepsilon(\infty)\sqrt{N}} \left( \sum_l e^{ikR_l} \right) \sum_{j\neq0} e^{ikR_j} \vec{\nabla}_{R_j}
\]

\[
\times \left( \frac{e^{-2\alpha R/a_0}}{R} \left( 1 + \frac{\alpha R}{a_0} \right) \right)_{R=R_j} = \frac{ee^*}{4\pi \varepsilon(\infty)\sqrt{N}} \left( \sum_l e^{ikR_l} \right) \sum_{j\neq0} e^{ikR_j} \frac{e^{-2\alpha R_j/a_0}}{R_j^2}
\]

\[
\times \left( 1 + 2\alpha R_j/a_0 + 2\alpha^2 R_j^2/a_0^2 \right).
\]

The next step is to take \( \sum_k |\gamma_k|^2 \). There is a double sum over \((j, j')\). When \( l = l' \), the summation over \( k \) forces \( R_j = R_{j'} \). The final answer for \( l = l' \) is

\[
V''_{pp} = -\frac{e^2(e^*)^2}{2\varepsilon(\infty)^2} \sum_{j\neq0} e^{-2\alpha R_j/a_0} R_j^2
\]

\[
\times \left( 1 + 2\alpha R_j/a_0 + 2\alpha^2 R_j^2/a_0^2 \right)^2.
\]

This answer is only slightly different than case number 1. The summation over \( R_j \) converges to a finite value. There is no ionized donor energy as in Eq. (27). That is sensible, since the neutral donor should not attract long-range polarization.

We rewrite the above expression using the nearest-neighbor distance \( d \) as a unit of length,

\[
V''_{pp} = -E_{RY} \frac{\omega_d^2}{\omega_{LO}^2} F(\alpha d/a_0),
\]

\[
F(\alpha d/a_0) = \frac{\Omega_0 d}{4\pi} \sum_{j\neq0} e^{-4\alpha R_j/a_0} R_j^2 \times \left( 1 + 2\alpha R_j/a_0 + 2\alpha^2 R_j^2/a_0^2 \right)^2.
\]

An important result is the screening energy of the ionized donor, which is found by setting \( a_0 = \infty \),

\[
V' = -\frac{e^2}{8\pi \varepsilon(\infty)d} \left( \frac{e^2}{\varepsilon(\infty)K_L \Omega_0} \right)^2 F(0).
\]

This formula is exact and is an improvement to Eq. (27). For the fcc lattice, \( F(0) = 1.425780 \) using Ewald methods, which are described in the Appendix. By comparing the two expressions, we determine that

\[
\tilde{a} = a \sqrt{\frac{\sqrt{3}}{F(0)}} = 0.992a.
\]

The energy of the ionized donor must be subtracted from the result of Eq. (53), which gives the final donor binding energy,

\[
\mathcal{E}(\alpha) = E_{RY} \left[ (\alpha^2 - 2\alpha - \eta) F(\alpha d/a_0) - F(0) \right],
\]

\[
\eta = \frac{\left( \frac{e^2}{\varepsilon(\infty)K_L \Omega_0} \right)^2}{\frac{a_0 \omega_d^2}{\omega_{LO}^2}}.
\]

For a given crystal structure, \( F(x) \) is a function of \( x = \alpha d/a_0 \). The self-consistent variational equation for the coupling constant \( a_0 \) at minimum energy is

\[
a_0 = 1 + \frac{1}{2} \frac{\omega_d^2}{\omega_{LO}^2} F'(x)_{x=a_0d/a_0},
\]

where \( F'(x) = dF/dx < 0 \).

For many semiconductors, the value of \( x \) is small, and it is adequate to take the limit of small \( x \),

\[
F(x) - F(0) = x F'(0) + O(x^3).
\]

Using Ewald methods, we show for the fcc lattice that \( F'(0) = -11/8 \), which makes Eq. (57) identical to Eq. (43). The derivation in the Appendix suggests that this result \( F'(0) = -11/8 \) is valid for all lattices. For weakly bound donors, our two derivations give the same result. Equations (57) and (59) are useful for materials with larger values of \( x \).

D. Atomic limit for donor

One case is when the donor is tightly bound, so that \( d/a_0 > 1 \). Even then, the term \( F(x) \) is not small and cannot be neglected. For example, \( F(1) = 0.35 \).

E. Ferroelectrics

Many ferroelectrics have the feature in which as one nears the transition temperature \( T_c \), \( \varepsilon(0) \) diverges, while \( \varepsilon(\infty) \) remains constant. This is the result of \( \omega_{pF} \) going to zero, while \( \omega_{LO} \) remains constant. In our first model, as \( \omega_{pF} \rightarrow 0 \), then \( \omega_{LO} \rightarrow \omega_1 \). The donor binding energy does not vanish, but is given by \( E_{RY}(5/16)^2 \approx 0.1 E_{RY} \).
V. FCC LATTICE

We present some calculations for the fcc lattice, where \( d = a/\sqrt{2} \) and \( \Omega_0 = a^3/4 = d^3/\sqrt{2} \). We discuss the evaluation of the function \( F(x) \), in Eq. (54), and its derivative \( F'(x) \),

\[
F(x) = \frac{\Omega_0 d}{4\pi} \sum_{j \neq 0} \frac{e^{-4\pi R_j/d}}{R_j^2} \left[ 1 + 2x R_j/d + 2x^2 (R_j/d)^2 \right].
\]

We define the summation variable as \( y_j = R_j/d \), which starts out as one for the 12 nearest neighbors,

\[
F(x) = \frac{1}{4\pi \sqrt{2}} \sum_{j \neq 0} \frac{e^{-4\pi y_j}}{y_j^2} (1 + 2x y_j + 2x^2 y_j^2)^2.
\]

One way to evaluate Eq. (62) is to sum all neighbors out to a distance \( y_j \). However, the expression converges very slowly for small values of \( x \). We performed the computer summations out to a distance \( y_j \) and noticed that they seem to scale as \(-1/y_j\). We did a least-squares fit to the expression \( F(0) = C - B/y_j \), which gave \( C = 1.425781 \), which is very close to the Ewald result. Using Ewald methods in the Appendix, we obtain the same value.

A similar process determines \( F'(x) \):

\[
F'(x) = -\frac{8x^2}{4\pi \sqrt{2}} \sum_{j \neq 0} \frac{e^{-4\pi y_j}}{y_j^2} (1 + 2x y_j + 2x^2 y_j^2).
\]

Using Ewald methods, we found the exact expression \( F'(0) = -11/8 \). In the Appendix, we derive the next terms in the power series in \( x \),

\[
F(x) = F(0) - \frac{11}{8} x + \frac{B}{3} x^3 + O(x^4),
\]

where \( B = 1.4595 \). With these values, we constructed the graph of \( F(x) \) shown in Fig. 1.

The eigenvalue equation (59) involves the function \( F'(x) \), which we have evaluated from Eq. (63). For fitting purposes, it is useful to have an analytic function that approximates these numerical values. The following expression is accurate to \( O(0.3\%) \):

\[
F'(x) \approx -\frac{24x^2}{\pi \sqrt{2}} \left[ e^{-4\pi x} (1 + 2x + x^2) - e^{-1.3\xi x} \right] + B x^2 e^{-3x}
\]

\[
-\frac{11}{8} x + \frac{x}{2} \left[ 1 + \xi x + \frac{1}{2} (\xi x)^2 \right],
\]

where \( B \) is defined above, and the fitting parameter is \( \xi = 5.09490 \). The first term on the right is the asymptotic limit from the nearest-neighbor contribution in Eq. (63).

We have used our theory to calculate the donor binding energies in several crystals, as shown in Table I. The data are from Landolt-Börnstein.\(^1\) Only cubic crystals are included, and only those whose conduction-band minimum is at the center of the Brillouin zone, so the effective mass is isotropic. For the oxides, the binding is sufficiently large that we solved Eq. (59) self-consistently. This gives a much larger binding energy compared to the SHM. Both our theory and the SHM are poor for the oxides, since electrons are too tightly bound for effective mass theory to be valid. We show these results only to demonstrate that for large values of \( x \), our theory is different than the SHM.

As stated in Sec. I, we regard our theory as a strong-coupling result, which is valid when the dielectric functions \( \varepsilon(\infty) \) and \( \varepsilon(0) \) are very different. This is not the case for most III-V semiconductors, and our theory does not do well for these materials. However, we expect our theory to apply quite well to the II-VI semiconductors, which are generally more polar than the III-V semiconductors. Table I shows our theory does relatively well for these materials.

VI. DISCUSSION

We have evaluated the polaron corrections to the binding energy of electrons to donors. We include the following interactions: electron-phonon, donor-phonon, and phonon-phonon. Two variational calculations gave identical results in the limit of a small binding energy. For the case of a large binding energy, one method is exact but gives an equation for the variational parameter that must be solved self-consistently.
Most textbooks give the donor binding energy as
\[ E_D = -\frac{e^4 m}{2(4\pi \varepsilon(0))^2 \hbar^2}, \tag{66} \]
where \( m \) is the band effective mass of the electron and \( \varepsilon(0) \) is the static dielectric function. We get a different expression,
\[ E_D = -\frac{e^4 m}{2(4\pi \varepsilon)^2 \hbar^2}, \tag{67} \]
\[ \frac{1}{\varepsilon} = \frac{5}{16\varepsilon(\infty)} + \frac{11}{16\varepsilon(0)}, \tag{68} \]
which includes both dielectric constants \([\varepsilon(\infty), \varepsilon(0)]\). The effective Bohr radius is \( \bar{a}_0 = 4\pi \bar{\varepsilon} \hbar^2 / me^2 \). We expect our theory applies in the strong-coupling limit, when \( \varepsilon(\infty) \) and \( \varepsilon(0) \) are very different.

There is also the question of whether the effective mass \( m^* \) includes polaron corrections or is just the bare band mass. In our theory, it is the bare band mass. The above equation applies only to the case of \( E_D < \hbar^2 a_0^2 / 2m \). For materials with larger binding energies, one must solve a nonlinear equation to determine the parameters of the binding energy. We used our theory to calculate the donor binding energy of several materials with the fcc crystal structure.

One might consider a similar calculation for the electronic polaron effects; the terms that make \( \varepsilon(\infty) \) differ from \( \varepsilon(0) \). Here one would start with a bare interaction, screened by the vacuum dielectric constant \( \varepsilon_0 \), and consider how the electronic screening changes the donor binding energy. That is a different calculation than we have done here, since the electronic screening is in different places in the crystal. For the oxides, and other ionic crystals, the electronic polarization resides mostly with the anions.\(^{19}\) However, for covalent materials, it resides in the bonds between ions.

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**APPENDIX: EWALD SUMMATION**

The functions \( F(x), F'(x) \) are evaluated using an Ewald method.\(^{20}\) We start with an evaluation of \( F(0) \) since it is easy:
\[ F(0) = \frac{\Omega_0 q d}{4\pi} \sum_{j \neq 0} \frac{1}{R_j} = \frac{\Omega_0 q d}{4\pi} \sum_{j \neq 0} \int_0^\infty dt \exp(-t^2 R_j^2), \tag{A1} \]
\[ = F_L + F_R. \tag{A2} \]
\[ F_L = \frac{\Omega_0 q d}{4\pi} \sum_{j \neq 0} \int_0^\infty dt \exp(-t^2 R_j^2), \]
\[ = \frac{\Omega_0 q d}{4\pi} \sum_{j \neq 0} \frac{1}{R_j} \exp(-\eta^2 R_j^2) [1 + (\eta R_j)^2], \tag{A3} \]
\[ F_R = \frac{\Omega_0 q d}{4\pi} \sum_{j \neq 0} \int_0^\infty dt \exp(-t^2 R_j^2), \tag{A4} \]
where \( \eta = C/\bar{a} \). The term \( F_L \) we leave as is, since it converges rapidly in real space. The term \( F_R \) is changed to a summation over reciprocal lattice vectors by creating a periodic function of position \( \mathbf{r} \),
\[ V_R(\mathbf{r}) = 2 \sum_j \int_0^\infty dt \exp(-t^2 |\mathbf{R}_j - \mathbf{r}|^2) = \sum_G v(G)e^{i\mathbf{G} \cdot \mathbf{r}}, \tag{A5} \]
\[ v(G) = \frac{2}{\Omega_0} \int_0^\infty t^2 dt \int d^3r e^{i\mathbf{G} \cdot \mathbf{r}} e^{-t^2 r^2}, \tag{A6} \]
\[ v(G) = \frac{2\pi^{3/2}}{\Omega_0} \int_0^\infty dt \exp(-t^2 \mathbf{G}^2 / 4m^2) = \frac{\Omega_0}{\Omega_0} \int_0^{2\eta/\mathbf{G}} dxe^{-x^2/2}, \tag{A7} \]
\[ F_R = \frac{\Omega_0 q d}{4\pi} \left[ \frac{2\pi^{3/2} \eta}{\Omega_0} + \sum_{G \neq 0} v(G) \eta^2 \right]. \tag{A8} \]

The first term in \( F_R \) is the \( v(\mathbf{G}) \), and the last term is from the subtraction of the \( \mathbf{R}_j = 0 \) term from \( V_R(\mathbf{r}) \). Table II shows the separate contributions as a function of \( C \). The final result is independent of \( C \), which is a good way to check the computer code.

Next, we determine \( F'(0) \) starting from Eq. (63). Since the prefactor is proportional to \( \sqrt{x} \), we must take the limit of \( x \to 0 \) with some care. We use Ewald’s method with an exponential,
\[ \frac{1}{\eta y_j} = \int_0^\infty dte^{-t(y_j)^2} = \int_0^\infty dt e^{-t(y_j)^2} + \int_\eta^\infty dte^{-t(y_j)^2}, \tag{A9} \]
\[ F_L(x) = -\frac{8\pi^2}{4\pi \sqrt{2}} \sum_{j \neq 0} e^{-y_j (\eta x + \eta)} (1 + 2xy_j + 2x^2 y_j^2), \tag{A10} \]
\[ F_R(x) = -\frac{8\pi^2}{4\pi \sqrt{2}} \int_0^\infty dt \sum_{j \neq 0} e^{-y_j (\eta x + \eta)} (1 + 2xy_j + 2x^2 y_j^2). \tag{A11} \]

The lattice sum vanishes at \( x = 0 : F_L'(0) = 0 \). We evaluate \( F_R'(x) \) by constructing a periodic function of \( \mathbf{r} \) and then determining its Fourier coefficient,
\[ V_R(\mathbf{r}) = \sum_j e^{-i\mathbf{G} \cdot (\eta x + \eta)} [1 + 2xy_j - \mathbf{r}] + 2x^2 (y_j - \mathbf{r})^2 \]
\[ = \sum_G e^{i\mathbf{G} \cdot \mathbf{r}} v(G), \]
\[ v(G) = \frac{1}{\Omega_0} \int d^3r \exp[-i\mathbf{G} \cdot \mathbf{r} - r(4x + t)] \times [1 + 2x \eta + 2x^2 r^2], \tag{A12} \]
\[ v(G) = 8\pi \sqrt{2} \left[ \frac{\tau}{(\tau^2 + G^2)^3} + 2x \frac{3\tau^2 - G^2}{(\tau^2 + G^2)^3} \right], \tag{A13} \]
\[ \tau = 4x + t. \tag{A14} \]
The result for $F'(0)$ comes from the term with $G = 0$. This integral is easy to evaluate:

$$v(0) = 8\pi \sqrt{2} \left[ \frac{1}{\tau^3} + \frac{6x}{\tau^4} + \frac{24x^2}{\tau^5} \right],$$

(A15)

$$\int_0^\eta dt v(0) = 8\pi \sqrt{2} \left[ \frac{1}{2} \left( \frac{1}{16x^2} - \frac{1}{(4x + \eta)^2} \right) + 2x \left( \frac{1}{(4x)^3} - \frac{1}{(4x + \eta)^3} \right) + 6x^2 \left( \frac{1}{(4x)^4} - \frac{1}{(4x + \eta)^4} \right) \right].$$

(A16)

The terms in the above equation, which are proportional to $O(x^{-2})$, give the limit as $x \to 0$,

$$F'(0) = -\frac{8}{\eta} \left( 1 + 1 + \frac{3}{4} \right) = -\frac{11}{4}.\tag{A17}$$

One can also use the Ewald sum to find the first nonzero term in $x$, which is

$$F'(x) = -\frac{11}{8} + Bx^2 + O(x^3),$$

(A18)

$$B = -\frac{\sqrt{2}}{\pi} \sum_{j \neq 0} e^{-\gamma_j \eta} \frac{\eta}{y_j} + \frac{8}{\eta^2} + \frac{8\eta}{4\pi \sqrt{2}} - \frac{8}{G^2(G^2 + \eta^2)},$$

(A19)

which gives $B = 1.4595 \pm 0.0001$.