

Simplified electrostatic model for band-gap underestimates in the local-density approximation

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An estimate of the undercounted electrostatic energy terms in local-density-functional total-energy calculations for nonmetallic systems with separated electron-hole pairs is used to derive a simplified correction to density-functional-theory band gaps. The correction is evaluated for Ne, Ar, Kr, LiF, NaCl, CsCl, MgO, CaS, BaS, C, AlP, and Si. The band-gap errors are reduced from 40–50 % to 10–15 % for most of the systems studied. Conduction-band corrections are shown to be nearly as large as valence-band corrections in free-electron-like semiconductors.

I. INTRODUCTION

The applicability of density-functional (DF) theory to the calculation of excitation energies in semiconductors and insulators has recently received intense scrutiny.^{1–9} It is by now generally believed that DF theory can produce correct band gaps,¹⁰ since these are differences between total energies of ground states of systems having different numbers of electrons. However, even with the exact DF one-electron ground-state potential, excitation energies in insulators cannot be expressed directly as differences between one-electron eigenvalues, since the potential changes discontinuously across the band gap.^{1,2} Thus gradient corrections and other methods for obtaining DF potentials more accurate than those given by the local-density approximation (LDA) can alleviate only a small part of the 40–50 % band-gap underestimates caused by the LDA. Methods proposed for obtaining gaps superior to the LDA gaps include the use of (1) frequency-dependent self-energies based on approximate dielectric functions, which have achieved promising results for C and Si,^{3,5} (2) orbital-dependent self-interaction corrections,^{7,8,11,12} which have produced accurate band gaps for narrow-band insulators, and (3) screened empirically obtained atomic-interaction parameters.⁹

In this paper we propose a physically transparent model for the LDA band-gap discrepancies which applies to a wide variety of solids, ranging from free-electron-like semiconductors to narrow-band insulators. Rather than attempting to calculate the correct frequency-dependent quasiparticle potential for valence- and conduction-band states, we focus directly on estimating the LDA underestimate of the total energy for a system containing a separated electron-hole pair. We favor this approach because density-functional theory is primarily aimed at obtaining correct total energies and charge densities, rather than quasiparticle potentials. As is pointed out in Ref. 13, the use of the LDA implicitly assumes that the exchange-correlation hole surrounding an electron is complete, i.e.,

$$\int d\mathbf{r}' [\langle n(\mathbf{r})n(\mathbf{r}') \rangle - \langle n(\mathbf{r}) \rangle \delta(\mathbf{r}-\mathbf{r}') - \langle n(\mathbf{r}) \rangle \langle n(\mathbf{r}') \rangle] = -\langle n(\mathbf{r}) \rangle \quad (1)$$

for all \mathbf{r} . Here $n(\mathbf{r})$ is the electron number density operator. Equation (1) is satisfied in any many-electron system, provided that the integral is taken over a region including the *whole* system. In the uniform electron gas systems used to obtain the LDA one-electron potential, the sum rule (1) is actually exhausted over a distance of a few interelectron spacings. This is also expected to be true in atoms, molecules, metals, and insulators without free carriers, which is consistent with the success of the LDA in calculating ground-state properties in these systems. However, in insulators with free carriers it is necessary to take the integral over a region whose volume is comparable to the volume per carrier in order to exhaust the sum rule. Thus we expect errors to result from the application of the LDA to such systems. It will be shown that the extra electrostatic energy associated with the incompleteness of the exchange-correlation hole can in fact explain a large part of the LDA band-gap underestimates.

II. DERIVATION OF MODEL

We obtain a simple estimate of the extra electrostatic energy due to the incompleteness of the exchange-correlation hole, beginning for simplicity with the case of a Bravais lattice of atoms sufficiently widely spaced that the crystal charge density is practically indistinguishable from the atomic charge density. The fluctuating part of the electron-electron interaction energy is given by

$$U_{xc} = \frac{e^2}{2} \int \frac{[p(\mathbf{r}, \mathbf{r}'; t=0) - \langle n(\mathbf{r}) \rangle \langle \delta(\mathbf{r}-\mathbf{r}') \rangle]}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} d\mathbf{r}' ,$$

where

$$\begin{aligned} p(\mathbf{r}, \mathbf{r}', t) &= \frac{1}{2} \langle \{ n(\mathbf{r}, t), n(\mathbf{r}', 0) \} \rangle - \langle n(\mathbf{r}) \rangle \langle n(\mathbf{r}') \rangle \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \tilde{p}(\mathbf{r}, \mathbf{r}'; \omega) e^{-i\omega t} , \end{aligned}$$

defining \tilde{p} . If there are no free carriers in the system, then the lowest-lying excitations of the system are exciton states, and the characteristic frequency scale associated

with $p(\mathbf{r}, \mathbf{r}'; t)$ is an atomic frequency ω_{at} . However, if a single free quasiparticle is present, another frequency $\omega_{\text{band}} \ll \omega_{\text{at}}$ appears, which is associated with intraband transitions between different Bloch quasiparticle wave

states. We expect the errors induced by the LDA to be most pronounced for the energy $U_{\text{xc},0}$ associated with the slower frequency scale, and thus focus on estimating $U_{\text{xc},0}$. If ω_0 satisfies $\omega_{\text{band}} \ll \omega_0 \ll \omega_{\text{at}}$, then

$$U_{\text{xc},0} \approx \frac{e^2}{2} \int \left[\int_{-\omega_0}^{\omega_0} \frac{d\omega}{2\pi} \tilde{p}(\mathbf{r}, \mathbf{r}'; \omega) \right] \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \frac{e^2}{2} \int \left[\int_{-\infty}^{\infty} \frac{dt}{\pi t} \sin(\omega_0 t) p(\mathbf{r}, \mathbf{r}'; t) \right] \frac{1}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\ \approx \frac{e^2}{2} \int \frac{p(\mathbf{r}, \mathbf{r}'; t_0)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

where

$$\omega_{\text{at}}^{-1} \ll t_0 \ll \omega_{\text{band}}^{-1}. \quad (2)$$

A straightforward calculation shows that if t_0 satisfies (2), so that the quasiparticle may be regarded as stationary, then

$$\langle n(\mathbf{r}) \rangle = n_{\text{at}}(\mathbf{r} - \mathbf{R}) + \frac{1}{N} \delta n_{\text{at}}(\mathbf{r} - \mathbf{R})$$

and

$$\frac{1}{2} \langle \{n(\mathbf{r}, t_0), n(\mathbf{r}', 0)\} \rangle = \left[1 - \frac{1}{N} \right] n_{\text{at}}(\mathbf{r} - \mathbf{R}) n_{\text{at}}(\mathbf{r}' - \mathbf{R}') \\ + \frac{1}{N} [n_{\text{at}}(\mathbf{r} - \mathbf{R}) + \delta n_{\text{at}}(\mathbf{r} - \mathbf{R})] [n_{\text{at}}(\mathbf{r}' - \mathbf{R}') + \delta n_{\text{at}}(\mathbf{r}' - \mathbf{R}')] \text{ if } \mathbf{R} = \mathbf{R}' \\ = \langle n(\mathbf{r}) \rangle \langle n(\mathbf{r}') \rangle - \frac{1}{N^2} \delta n_{\text{at}}(\mathbf{r} - \mathbf{R}) \delta n_{\text{at}}(\mathbf{r}' - \mathbf{R}') \text{ otherwise.}$$

Here \mathbf{R} is the position of the nucleus closest to \mathbf{r} , n_{at} is the atomic electron density, N is the number of atoms in the system, and δn_{at} is N times the charge-density change associated with the quasiparticle, so that

$$\int_{\text{atomic cell}} \delta n_{\text{at}}(\mathbf{r}) d\mathbf{r} = \begin{cases} 1 & (\text{electron}) \\ -1 & (\text{hole}) \end{cases}$$

Thus, to order $1/N$,

$$p(\mathbf{r}, \mathbf{r}'; t_0) = \begin{cases} \frac{1}{N} [\delta n_{\text{at}}(\mathbf{r} - \mathbf{R}) \delta n_{\text{at}}(\mathbf{r}' - \mathbf{R}')] & \text{if } \mathbf{R} = \mathbf{R}', \\ 0 & \text{otherwise} \end{cases}$$

and

$$U_{\text{xc},0} = \frac{e^2}{2} \int_{\text{atomic cell}} \frac{\delta n_{\text{at}}(\mathbf{r}) \delta n_{\text{at}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (3)$$

In the LDA it is assumed that δn_{at} is screened within a metallic screening length and screening time, so that the LDA charge-density change $\delta n_{\text{at}}^{\text{LDA}}$ satisfies

$$\int_{\text{atomic cell}} \delta n_{\text{at}}^{\text{LDA}}(\mathbf{r}) d\mathbf{r} = 0.$$

$U_{\text{xc},0}$ is therefore obtained incorrectly. To estimate the LDA error in $U_{\text{xc},0}$, we estimate the LDA screening electron density δn_{scr} as follows:

$$\delta n_{\text{scr}}(\mathbf{r}) = \bar{n} \int d\mathbf{r}' [g(|\mathbf{r} - \mathbf{r}'|; \bar{n}) - 1] \delta n_{\text{at}}(\mathbf{r}').$$

Here $g(|\mathbf{r} - \mathbf{r}'|; \bar{n})$ is the pair distribution function for a

uniform electron gas having the weighted average density

$$\bar{n} = \left| \int \delta n_{\text{at}}(\mathbf{r}) n_{\text{at}}(\mathbf{r})^{1/3} d^3r \right|^3.$$

(We average $n_{\text{at}}^{1/3}$ rather than n_{at} because the screening energy is nearly proportional to $n_{\text{at}}^{1/3}$.) We further approximate the pair distribution function by $g(|\mathbf{r} - \mathbf{r}'|; \bar{n}) - 1 = -e^{-\kappa|\mathbf{r} - \mathbf{r}'|}$, where $\kappa = (8\pi\bar{n})^{1/3}$. This form for g guarantees that $|\int \delta n_{\text{scr}}(\mathbf{r}) d\mathbf{r}| = 1$ and that $g(0, \bar{n}) = 0$; the latter condition is well satisfied in electron gases at typical valence electron densities.¹⁴ The error in $U_{\text{xc},0}$ due to the LDA is then

$$\Delta U_{\text{xc},0} = \frac{e^2}{2} \\ \times \int d\mathbf{r} d\mathbf{r}' \frac{[\delta n_{\text{at}}^{\text{LDA}}(\mathbf{r}) \delta n_{\text{at}}^{\text{LDA}}(\mathbf{r}') - \delta n_{\text{at}}(\mathbf{r}) \delta n_{\text{at}}(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|} \quad (4)$$

where $\delta n_{\text{at}}^{\text{LDA}} = \delta n_{\text{at}} + \delta n_{\text{scr}}$.

To treat the case of denser solids, we divide the electrostatic correction $\Delta U_{\text{xc},0}$ by the observed static electronic dielectric constant ϵ_0 . This procedure would be rigorously correct if $\Delta U_{\text{xc},0}$ resulted from a static external charge distribution having a very long wavelength (neglecting lattice contributions to screening). The neglect of the frequency and wave-vector dependence of the dielectric function should also be a reasonable approximation here because (1) we are primarily concerned with the low-frequency part of U_{xc} and (2) the discrepancy $\Delta U_{\text{xc},0}$ has its largest contributions at small wave vectors q . The

atom over which the integrals in (4) are performed is taken to be a unit cell, centered on the atom on which the level under consideration has the greatest amplitude; in cases such as Si and C in which the top of the valence band has equal amplitude on both of the atoms in the unit cell, one of the two equivalent nuclei is arbitrarily chosen as the center of the "atom." We approximate $\delta n_{\text{at}}(\mathbf{r})$ by

$$\Delta_{v,c} = \frac{e^2}{2\epsilon_0} \int_{\text{unit cell}} d\mathbf{r} d\mathbf{r}' \frac{[\delta n_{\text{at}}(\mathbf{r})\delta n_{\text{at}}(\mathbf{r}') - \delta n_{\text{at}}^{\text{LDA}}(\mathbf{r})\delta n_{\text{at}}^{\text{LDA}}(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|},$$

$$\delta n_{\text{at}}(\mathbf{r}) = \frac{|\psi_{v,c}(\mathbf{r})|^2}{\int_{\text{unit cell}} |\psi_{v,c}(\mathbf{r})|^2 d\mathbf{r}},$$

E_g^{LDA} is the LDA band gap, and $\psi_{v,c}(\mathbf{r})$ are the LDA wave functions for the quasi-hole and the quasihole. The correction is the *sum* of two positive contributions, coming from the incomplete screening of the electron and the hole. By contrast, in frequency-dependent self-energy methods,^{3,5} the correction is obtained as the *difference* between the self-energies in the valence and conduction bands.

The approach suggested here, while similar in spirit to that described in Ref. 9, differs in that no experimental input other than ϵ_0 is used, and that separate corrections for the valence and conduction bands are calculated. There are also formal similarities between Eq. (5) and the self-interaction correction^{7,8,11,12} (SIC). However, the physical assumptions underlying the derivation are quite different:

(1) We treat the conduction and valence bands on an equal footing. In the SIC method, the conduction-band corrections are assumed to be negligible. The numerical results to be discussed later indicate that Δ_c is comparable in magnitude to Δ_v , particularly in broadband semiconductors.

the square of the appropriate LDA wave function, normalized to the unit cell.

The corrected band gap is then given by

$$E_g = E_g^{\text{LDA}} + \Delta_v + \Delta_c, \quad (5)$$

where

(2) We emphasize the errors in the total energy of the excited *final* state containing an electron and a hole. The SIC method focuses on obtaining an accurate potential for valence-band electrons in the ground state.

(3) In extensions of the SIC method to solids, the atomic wave functions have generally been replaced by Wannier functions derived from the Bloch waves.⁷ Because we emphasize the underestimate of the electron-electron interaction energy in the LDA, we instead focus on the electrostatic screening effects due to the solid environment.

III. RESULTS

We have evaluated (5) for a wide variety of nonmetallic solids, ranging from atomiclike insulators to nearly-free-electron-like semiconductors: Ne, Ar, Kr, LiF, NaCl, CsCl, MgO, CaS, BaS, C, AIP, and Si. The systems studied are chosen (1) to sample each chemical group as completely as possible, but (2) to avoid complications due to relativistic effects.¹⁵ Thus GaAs, for example, is not included because the relativistic band energy shifts can be as

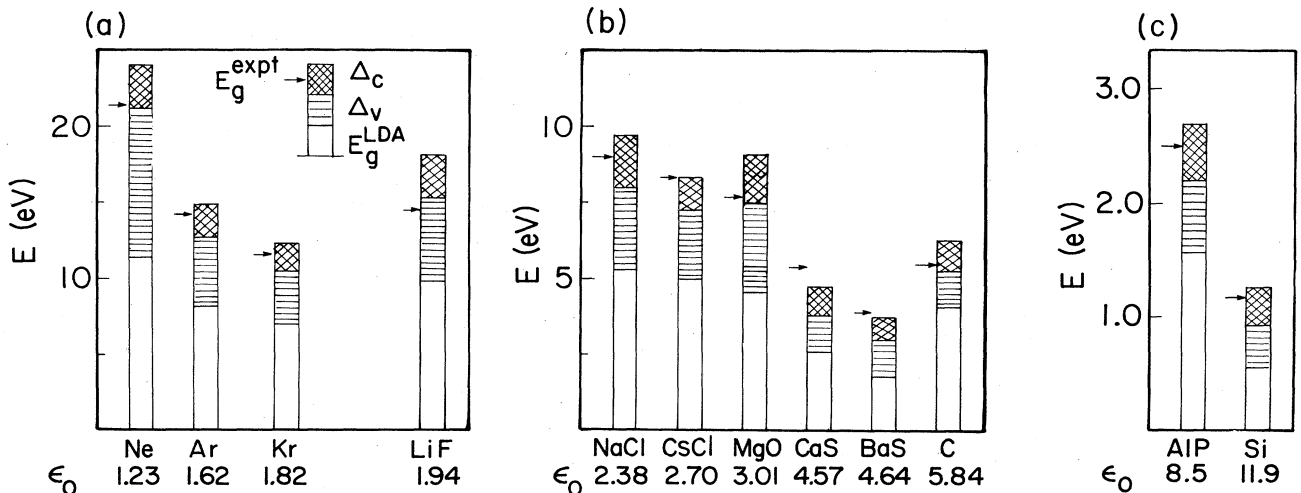


FIG. 1. Calculated valence- and conduction-band corrections Δ_v and Δ_c , LDA band gaps E_g^{LDA} , and experimental band gaps E_g^{expt} . The zero-wave-vector static electronic dielectric constant ϵ_0 (Ref. 25) is given for each substance.

large as half of the band gap.¹⁶ The calculations are performed using the self-consistent augmented-spherical-wave (ASW) method,¹⁷ with empty spheres used for the sodium chloride, zinc-blende, and diamond structures;^{18–20} when used in this fashion, the ASW method produces results in close agreement²¹ with those obtained using state-of-the-art band-structure methods. The Hedin-Lundqvist form of the exchange-correlation energy functional is used.²² Relativistic effects are neglected.

We have used an approximate scheme for evaluating the electrostatic integrals in (6), primarily because the approximations already made [such as the use of the static dielectric constant ϵ_0 and the restriction of the integrals in (6) to exactly one unit cell] are sufficiently crude to render improved accuracy in the electrostatic integrals of little value. In this scheme the charge from the ASW spheres other than the central sphere is approximated by spherical shells with suitably chosen radii.²³ We estimate²⁴ that this procedure causes errors of $\lesssim 10\%$ in (6); since (6) is typically only half of the band gap, the resulting error in the gap is $\lesssim 5\%$.

The results²⁵ for Δ_v and Δ_c are shown graphically in Fig. 1 along with the LDA band gaps²⁶ E_g^{LDA} and the experimentally determined gaps²⁷ E_g^{expt} . In each case Δ_c is less than but comparable to Δ_v , with the ratio Δ_c/Δ_v varying from 0.3 in Ne to 0.9 in Si. The smaller value of Δ_c is due to (1) the more diffuse charge density of the conduction-band wave functions and (2) the lower valence charge density in the spatial regions where the conduction-band wave functions are concentrated. These differences are much less pronounced in free-electron-like semiconductors such as Si than in atomlike insulators such as Ne.

The electrostatic correction $\Delta_v + \Delta_c$ significantly improves the agreement of the theoretical and experimental gaps. Most of the discrepancies are reduced from

40–50% to 10–15%. The corrections are systematically overestimated, in part because relaxation effects are underestimated by the use of LDA wave functions in calculating $\Delta_v + \Delta_c$ [cf. Eq. (6)]. The results for Ne, LiF, MgO, and C, all of which contain atoms in the first row of the Periodic Table, are worse than for the remaining systems. The difficulties with the first row atoms are probably due to their highly localized $2p$ valence orbitals, for which the LDA is a bad starting point. However, the overall improvement in the calculated gaps for the wide variety of solids studied here suggests that the physical effects included in the model are in fact the dominant ones.

Achieving the utmost accuracy in excitation energies will undoubtedly require elaborate many-body calculations building on the techniques developed in Refs. 2–6. However, the simplicity of the model described here provides easy interpretability and enables one to study broad classes of systems with comparatively little computational effort. It would be desirable to apply the model to pressure-induced band-overlap metallization and other problems in which ϵ_0 is not known. This will require a self-consistent calculation of ϵ_0 from the quasiparticle band structure (which in turn is affected by ϵ_0). Successful calculations²⁸ of the dielectric functions of semiconductors, based on semiempirically obtained band structures, indicate that this task is feasible.

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¹J. P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).

²L. J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888 (1983).

³C. S. Wang and W. A. Pickett, Phys. Rev. Lett. **51**, 597 (1983);
W. A. Pickett and C. S. Wang, Phys. Rev. B **30**, 4719 (1984).

⁴Z. H. Levine and S. G. Louie, Phys. Rev. B **25**, 6310 (1982).

⁵W. Hanke, Th. Gölzer, and H. J. Mattausch, Solid State Commun. **51**, 23 (1984).

⁶W.-D. Lukas and P. Fulde, Phys. Rev. B **30**, 757 (1984).

⁷R. A. Heaton, J. G. Harrison, and C. C. Lin, Phys. Rev. B **28**, 5992 (1983).

⁸J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

⁹W. A. Harrison, Phys. Rev. B **31**, 2121 (1985).

¹⁰A. R. Williams and U. von Barth, in *Theory of the Inhomogeneous Electron Gas*, edited by S. Lundqvist and N. H. March (Plenum, New York, 1983).

¹¹A. B. Kunz, R. S. Wiedman, J. Boettger, and G. Cochran, Int. J. Quantum Chem. Symp. **14**, 585 (1980).

¹²I. Lindgren, Int. J. Quantum Chem. Symp. **5**, 411 (1971).

¹³O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

¹⁴See, for example, P. Vashishta and K. S. Singwi, Phys. Rev. B **6**, 875 (1972).

¹⁵Although the Ba $6s$ level is very sensitive to relativistic effects, the band gap of BaS is much less sensitive since neither the Γ_{15} state at the valence-band upper edge nor the X_3 state at the conduction-band lower edge have s -type symmetry about the Ba site. The Ba $5d$ orbital which is the major constituent of the X_3 state is insensitive to relativistic effects.

¹⁶G. B. Bachelet and N. E. Christensen, Bull. Am. Phys. Soc. **29**, 349 (1984).

¹⁷A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. B **19**, 6094 (1979).

¹⁸D. Glötzel, B. Segall, and O. K. Andersen, Solid State Commun. **36**, 403 (1980).

¹⁹T. Jarlborg and A. J. Freeman, Phys. Lett. **74A**, 349 (1979).

²⁰The atomic sphere radii for the solids with more than one atom per unit cell were chosen as follows: For CsCl, the radii of the two atomic spheres in the unit cell were chosen equal. For the NaCl structure compounds, 30% of the unit-cell volume was assigned to each of the two atomic spheres in the unit cell, and 20% to each empty sphere. For the diamond and zinc-blende structure compounds, each of the spheres in the unit cell was assigned 25% of the unit-cell volume. This partitioning of space provides a reasonable compromise be-

tween (1) minimizing the sphere overlap volume, (2) maintaining the symmetry of the unit cell, and (3) accounting for the atomic core sizes. [P. A. Fedders and A. E. Carlsson (unpublished).]

²¹For example, with Hedin-Lundqvist (Ref. 20) exchange and correlation, the ASW gaps for Si, C (diamond), MgO, and LiF are 0.51, 4.11, 5.23, and 10.5 eV, respectively [P. A. Fedders and A. E. Carlsson (unpublished)]. The pseudopotential gaps for Si, C, and MgO are 0.56, 4.05 (Ref. 3), and 4.50 eV [K. J. Chang and M. L. Cohen, Phys. Rev. B **30**, 4774 (1984)]. For LiF, a self-consistent linear-combination-of-atomic-orbitals calculation with a slightly different exchange-correlation functional produces a gap of 9.9 eV [A. Zunger and A. J. Freeman, Phys. Rev. B **16**, 2901 (1977)].

²²L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

²³The radii \bar{r} are obtained as follows: First the averaged distance \bar{d} of the charge in each noncentral sphere from the center \mathbf{r}_{nc} of that sphere is computed, and the charge is placed on the fraction of a new shell of radius \bar{d} about \mathbf{r}_{nc} closest to the center \mathbf{r}_c of the central sphere. The fraction of the shell area used is the reciprocal of the number of spheres equivalent to the sphere under consideration. The radius \bar{r} is determined by setting $1/\bar{r}$ equal to the average value of $1/|\mathbf{r}-\mathbf{r}_c|$ on the part of the shell used.

²⁴The sphericalization of the charge density in the noncentral ASW spheres, about the center of the unit cell, underestimates the electrostatic integrals. We have obtained an estimate of the error by performing another electrostatic calculation: the charges in the noncentral ASW spheres are placed in new spheres, contained in the ASW spheres, with volumes substantially smaller than those corresponding to the fraction of the wave function's charge residing in the ASW spheres. This

procedure overestimates the electrostatic integrals. For the conduction-band lower edge in C, a large fraction (70%) of the charge density resides in the noncentral ASW spheres. We therefore expect the error resulting from the approximate treatment of the charge density in these spheres to be among the largest. Even in this case placing the noncentral sphere charges in spheres with volumes four times smaller than those corresponding to their charge fractions causes a discrepancy of only 10%.

²⁵ ϵ_0 for AIP is obtained from J. van Vechten, Phys. Rev. **182**, 891 (1969); the remaining values are taken from *CRC Handbook of Chemistry and Physics*, 63rd ed., edited by R. C. Weast and M. J. Astle (Chemical Rubber Co., Boca Raton, FL, 1982).

²⁶The gaps for Si and C are obtained from Ref. 3, that for MgO from Chang and Cohen (Ref. 21), while that for LiF is obtained from A. Zunger and A. J. Freeman (Ref. 21). The remaining gaps are obtained with the ASW method.

²⁷The values of E_g^{expt} are taken from U. Rössler, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1976), Vol. 1, p. 518 (Ne, Ar, and Kr); W. H. Strehlow and E. L. Cook, J. Phys. Chem. Ref. Data **2**, 163 (1973) (NaCl, MgO, BaS, CaS, and C); M. Piacentini, Solid State Commun. **17**, 697 (1975) (LiF); K. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967) (CsCl); B. Monemar, Phys. Rev. B **8**, 5711 (1973) (AIP); K. L. Shaklee and R. E. Nahory, Phys. Rev. Lett. **24**, 942 (1970) (Si). For CaS and BaS the measured absorption edges probably correspond most closely to the direct gap, and the calculations are therefore performed for the lowest predicted direct transitions.

²⁸J. P. Walter and M. L. Cohen, Phys. Rev. B **2**, 1821 (1970).