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Trends in self-energy operators and their corresponding exchange-correlation potentials

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We examine the trends in the self-energy operators of Si, diamond, GaAs, and AlAs, and in their corresponding exchange-correlation potentials V_{xc} and their discontinuities Δ. The potentials are calculated from the self-energies, thus avoiding use of a local-density approximation (LDA). In each case about 80% of the LDA band-gap error is also present for the true density-functional theory eigenvalue difference derived from V_{xc} and so is caused by Δ. The self-energies themselves, calculated in the Hedin-Lundqvist *GW* approximation, reproduce the experimental quasiparticle energies accurately, and are also shown to be well modeled by a simple functional form in real space.

In a previous paper[1] (hereafter referred to as I) we have shown how a relationship between the exact self-energy operator, $\Sigma(\mathbf{r},\mathbf{r}',\omega)$, of a system of electrons and the exact density-functional theory (DFT) exchange-correlation potential, $V_{\mathrm{xc}}(\mathbf{r})$, may be used to calculate an approximate V_{xc} from an approximate Σ. In the case of silicon, the V_{xc} obtained was very close to the local-density approximation $V_{\mathrm{xc}}^{\mathrm{LDA}}$, and about 80% of the error in the LDA minimum band gap (which is about half of the experimental quasiparticle gap) was also present in the band structure in which the "true"[2] V_{xc} is used. In this paper we examine how (i) the validity of the LDA, (ii) the forms of V_{xc} and Σ, and (iii) the **k** dependence of the quasiparticle energy corrections change between silicon, diamond, a more covalent material, and gallium arsenide and aluminum arsenide, both ionic semiconductors.

As in I, we use Hedin and Lundqvist's *GW* approximation to calculate the self-energy, where G is the one-particle Green's function (approximated by the LDA Green's function $G_{\mathrm{DFT}}^{\mathrm{LDA}}$) and where W is the screened Coulomb interaction, for which we use the random-phase approximation (RPA), including local-field effects and fully dynamical screening. V_{xc} is then calculated using an exact relationship[3] between Σ and V_{xc}. The DFT eigenvalues with the calculated V_{xc} and the quasiparticle energies are found using perturbation theory to second order in $\Sigma - V_{\mathrm{xc}}^{\mathrm{LDA}}$, which is observed to be well converged. In calculating the energy corrections, wave functions obtained from a nonlocal pseudopotential calculation are represented by 169 plane waves in 65 bands at ten **k** points in the irreducible wedge of the Brillouin zone.

In Table I we give various calculated quasiparticle and DFT energy gaps for the four materials, with the LDA and experimental gaps shown for comparison. Comparing the LDA and true DFT eigenvalue gaps shows that, surprisingly, the LDA remains a good approximation in gallium arsenide, aluminum arsenide, and diamond. In each case, 75–80% of the error in the LDA minimum band gap is also present with the true V_{xc}, and is therefore equal to the discontinuity $\Delta = V_{\mathrm{xc}}^{(N+1)} - V_{\mathrm{xc}}^{(N)}$ in V_{xc} when an electron is added to the N-electron semiconductor.[3,4] However, the absolute size of the discontinuity increases with the gap: 0.58 eV in silicon and 1.12 eV in diamond. The three calculated minimum gaps for each material are shown in Fig. 1 as a function of the experimental gap. The proximity of the *GW* and experimental gaps and of the V_{xc} and $V_{\mathrm{xc}}^{\mathrm{LDA}}$ gaps, and the substantial size of Δ are evident. Our quasiparticle calculations for AlAs suggest a new interpretation of the experimental data for the position of the indirect L conduction-band minimum in $\mathrm{Ga}_{1-x}\mathrm{Al}_x\mathrm{As}$ alloys, which will be reported elsewhere.[11] Core relaxation[12] and valence-core exchange and correlation[10] are terms of order 0.1–0.2 eV of opposite sign in GaAs and otherwise negligible.

We remarked in I that silicon's quasiparticle energies differ from the $V_{\mathrm{xc}}^{\mathrm{LDA}}$ eigenvalues (and therefore also those of V_{xc}) by a so-called *scissor operator*,[13] a rigid upward shift of the conduction bands. In contrast, the GaAs, AlAs, and especially diamond quasiparticle energies *cannot* be obtained from the LDA eigenvalues by such an operator. We therefore note not only that the *GW* approximation is capable of describing quasiparticle energy corrections beyond those of a rigid shift, but also that the procedure leading from Σ to the true V_{xc} can *undo* the nonrigidity of the energy corrections to give the close agreement between V_{xc} and $V_{\mathrm{xc}}^{\mathrm{LDA}}$.

We turn now to a discussion of the functional form of the self-energy $\Sigma(\mathbf{r},\mathbf{r}',\omega)$ in real space. The significant part of Σ resembles a single, almost spherically symmetric peak about $\mathbf{r}=\mathbf{r}'$ for each $\mathbf{r}$, where the peak func-

TABLE I. Direct gaps at Γ, *X*, and *L* and the minimum gap in silicon, diamond, GaAs and AlAs in (i) the LDA, (ii) the true DFT eigenvalues, (iii) the *GW* quasiparticle band structure, (iv) experiment, and (v) the difference *GW*-DFT. (i) is close to (ii), and (iii) to (iv).

Material	Gap	LDA^a	True DFT	*GW*	Expt.	*GW*-DFT
Si	Γ	2.57	2.68	3.30	3.40^b	0.62
	X	3.53	3.64	4.27	4.25^c	0.63
	L	2.75	2.83	3.49	3.3^d	0.66
	Min.	0.52	0.66	1.24	1.17^e	0.58^f
C	Γ	5.52^g	5.72	7.26	7.3^e	1.54
	X	10.84^g	11.07	12.55	12.5^e	1.48
	L	11.17^g	11.27	12.61		1.34
	Min.	3.90^g	4.21	5.33	5.48^e	1.12^f
GaAs	Γ	0.67^h	0.91^h	1.58^{h,i}	1.63^{j,e}	0.67
	X	4.06^h	4.14^h	4.83^{h,i}	5.19^{j,e}	0.69
	L	2.22^h	2.36^h	3.04^{h,i}	3.15^{j,e}	0.68
	Min.	0.67^h	0.91^h	1.58^{h,i}	1.63^{j,e}	0.67^f
AlAs	Γ	2.38	2.56	3.35	3.22^{j,e}	0.79
	X	3.54	3.72	4.48	4.64^{j,e}	0.76
	L	3.03	3.20	4.01	4.00^{j,e}	0.81
	Min.	1.37	1.55	2.18	2.32^{j,e}	0.63^f

[a] Ceperley-Alder LDA (Ref. 5).
[b] Reference 6.
[c] Reference 7.
[d] Reference 8 (experimental uncertainty ±0.2 eV).
[e] Reference 9.
[f] Equal to Δ, the discontinuity in V_{xc}: in each case about 80% of the LDA gap error.
[g] Reference 10.
[h] Pseudopotential calculation omits core relaxation—see text.
[i] Core-valence self-energy correction omitted—see text.
[j] Effect of spin-orbit splitting removed.

tion varies in amplitude but has approximately the same shape and range for each **r**. Figure 2 shows $\Sigma(\mathbf{r},\mathbf{r}')$ in silicon for **r** fixed at a bond center and in an interstitial site, and Fig. 3 shows the same quantities, averaged spherically, for each of the four materials. Moreover, the peak function is, to a good approximation, only multiplied by a constant factor when ω is varied by several electron volts. This suggests that Σ might be well modeled within this energy range by a function of the form

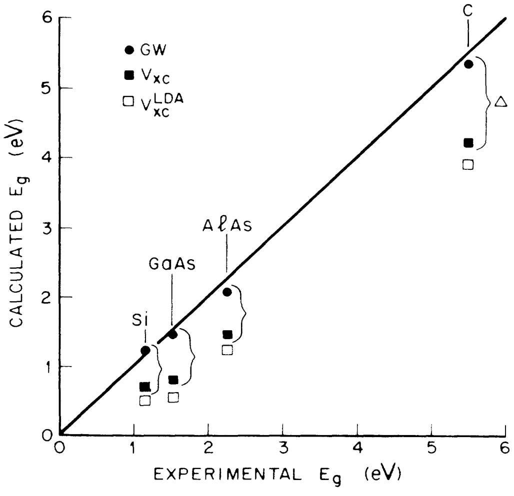

FIG. 1. The calculated minimum band gaps (corrected for spin-orbit splitting) with the *GW* self-energy and the true and LDA exchange-correlation potentials, plotted against the experimental $T=0$ minimum band gaps for the four materials. The 45° line is to guide the eye.

$$\Sigma(\mathbf{r},\mathbf{r}',\omega)\approx\tfrac{1}{2}[f(\mathbf{r})+f(\mathbf{r}')]g(\,|\mathbf{r}-\mathbf{r}'|\,)h(\omega)\ . \qquad (1)$$

To test this, we have fitted our calculated Σ to this form [using only the contribution to the **k**-point-averaged direct gap as a fitting parameter for each element of $f(\mathbf{r})$], and then recalculated the quasiparticle energies of silicon from the fitted form. We find that the energies are reproduced to within approximately 0.05 eV for all **k** points and all bands within 6 eV of the gap, which we consider to be an excellent fit.

The fitted functions $g(\,|\mathbf{r}-\mathbf{r}'|\,)$ and $h(\omega)$ are remarkably close to the equivalent functions for a *homogeneous* electron gas, whose *GW* self-energy was calculated by Hedin.[14] This is illustrated by the curves labeled *H* in Fig. 3, which show $\Sigma(\,|\mathbf{r}-\mathbf{r}'|\,,\bar{n},\omega=E_F)$, the self-energy of the homogeneous electron gas with density $\bar{n}$, the *average* density of the semiconductor.

Sham and Kohn[15] proposed the following local-density-like approximation for the self-energy:

$$\Sigma(\mathbf{r},\mathbf{r}',\omega)\approx\Sigma^{\text{hom}}(\,|\mathbf{r}-\mathbf{r}'|\,,n(\tfrac{1}{2}(\mathbf{r}+\mathbf{r}')),\omega)\ , \qquad (2)$$

where $n(\frac{1}{2}(\mathbf{r}+\mathbf{r}'))$ is the electron density halfway be-

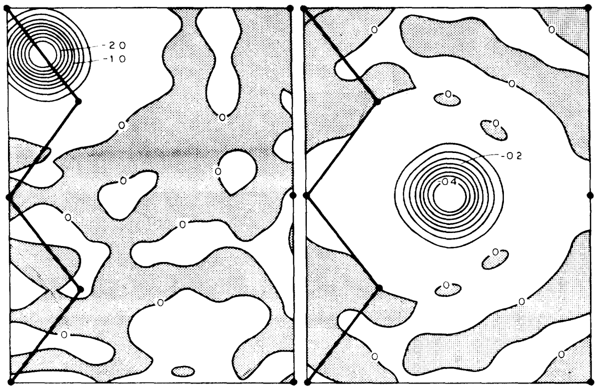

FIG. 2. Contour plots of $\Sigma(\mathbf{r},\mathbf{r}',\omega=\text{midgap})$ for silicon with $\mathbf{r}$ fixed at (a) a bond center and (b) the tetrahedral interstitial site, with $\mathbf{r}'$ shown in the (110) plane containing the bond chains as indicated.

tween $\mathbf{r}$ and $\mathbf{r}'$ and $\Sigma^{\text{hom}}(r,n,\omega)$ is the self-energy of a homogeneous electron gas with density n. In each case ω is measured relative to the chemical potential. Our results suggest a related but slightly different local-density-like approximation for Σ, in which the function $g(r)$ depends on the *average* density of the semiconductor, $\bar{n}$, not the *local* density halfway between $\mathbf{r}$ and $\mathbf{r}'$, and the density variation is reflected in the amplitude factor $f(\mathbf{r})$.

To our knowledge, the only attempt to implement the approximation of Ref. 15 was made by Wang and Pickett.[16] However, they chose to simplify the calculation by constraining Σ to be local:

$$\Sigma(\mathbf{r},\mathbf{r}',\omega)\approx\Sigma^{\text{hom}}(p(\mathbf{r}),n(\mathbf{r}),\bar{\omega})\delta(\mathbf{r}-\mathbf{r}') , \quad (3)$$

where p is the effective local wave vector and $\bar{\omega}$ is chosen to line up chemical potentials locally. Our finding, reported for silicon in I and now confirmed for gallium arsenide, aluminum arsenide, and diamond, that the range of the nonlocality of Σ is comparable with the wavelength of the wave functions of interest, shows that this assumption of locality cannot be valid for these materials. Nonlocality is essential.

We have traced the physical origin of the separable fgh model to the properties of the dielectric screening of the Coulomb interaction, $W=\epsilon^{-1}V$. If an unscreened V is used instead of W in the GW expression (which corresponds to the Hartree-Fock approximation), we find that Σ is extremely long-ranged in $|\mathbf{r}-\mathbf{r}'|$, as would be expected since a bare $1/r$ interaction now appears in Σ, and the model form (1) is no longer valid. Correspondingly, we find that the short-ranged $g(|\mathbf{r}-\mathbf{r}'|)$ behavior, approximately independent of $\mathbf{r}$, that we observe in Σ originates in the screened Coulomb interaction $W(\mathbf{r},\mathbf{r}',\omega)$. Σ, which is G times W in real space, acquires the range of the shorter ranged of the two, W. However, when W is replaced by the bare V for bare exchange, Σ is dominated by the range of G, which is considerably larger and much less isotropic.

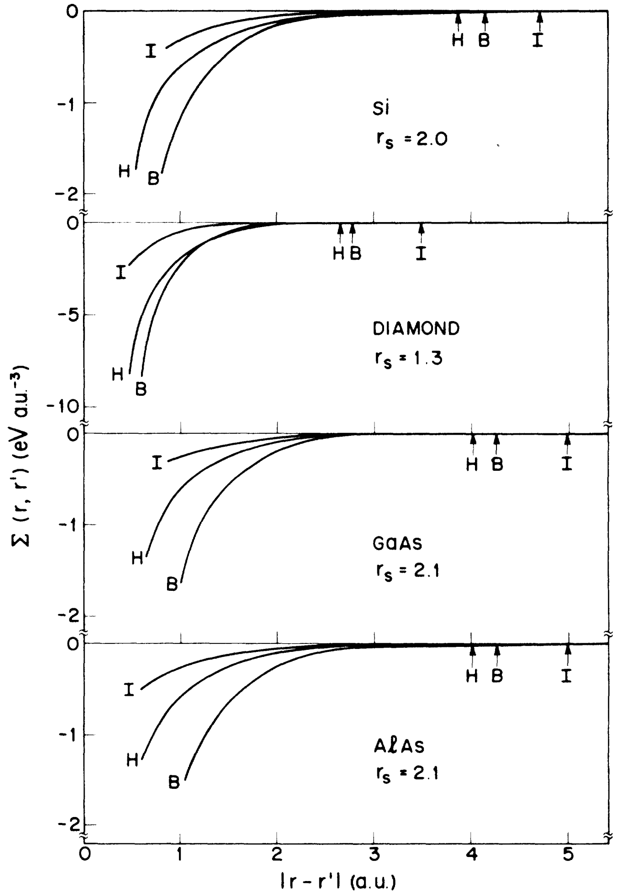

FIG. 3. Graphs of the spherical average of $\Sigma(\mathbf{r},\mathbf{r}',\omega=\text{midgap})$ for silicon, diamond, gallium arsenide, and aluminum arsenide with $\mathbf{r}$ fixed at a bond center (B) and the tetrahedral interstitial site (I). In each case the corresponding self-energy operator for jellium with the average density of the material (from Ref. 14) is also shown (H). The arrows indicate the positions of the zeros in the oscillatory functions Σ.

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[2] As before, we use "true V_{xc}" to mean the V_{xc} which corresponds to our calculated Σ through the exact relationship; if Σ is exact, this is the exact V_{xc}.

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