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BRIEF REPORTS

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Many-body effects on bandwidths in ionic, noble gas, and molecular solids

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Electron bandwidths in LiD, LiF, LiCl, solid C₆₀, MgO, KCl, Ar, and CaF₂, evaluated in the local-density approximation (LDA) and Hedin's *GW* approximation, are noted. Bandwidths are underestimated by the LDA as compared to *GW* results or experiment. This is explained by exchange and correlation effects being strongest on atomic or molecular sites, which compresses bands, with the LDA overestimating such compression. It is reasonable for compression to occur because states at the band maxima have more nodes between atoms or molecules, so that they are more concentrated on such sites. [S0163-1829(98)03036-7]

INTRODUCTION

To understand or predict optical properties and other characteristics of solids involving electron excitations, a description of the electron band states is often required. The local-density approximation¹ (LDA) and its gradient-corrected extensions² provide a useful theoretical framework for treating such states. Structural relaxation of solids can be carried out with ~1% accuracy using self-consistent LDA or gradient-corrected calculations. However, LDA band structures need corrections to account more accurately for exchange and correlation (self-energy) effects on band energies if the energies are to be used in conjunction with LDA wave functions to describe electron excitations. This work features a survey of self-energy effects on bandwidths in ionic, noble gas, and molecular solids. That is, a band considered is one derived from a complex of degenerate atomic or molecular orbitals, such as F 2*p* in LiF or the highest occupied *H_u* states in C₆₀.

To improve LDA band energies, quasiparticle calculations are often done.³⁻⁶ For a state in band *n* with crystal momentum **k**, the Dyson equation may be written

$$\begin{aligned} & [-\{\hbar^2/(2m)\}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r})]\Psi_{n\mathbf{k}}(\mathbf{r}) \\ & + \int d^3\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_{n\mathbf{k}}^{\text{qp}})\Psi_{n\mathbf{k}}(\mathbf{r}') = \epsilon_{n\mathbf{k}}^{\text{qp}}\Psi_{n\mathbf{k}}(\mathbf{r}). \end{aligned}$$

V_{ext} and V_H are the external potential (of nuclei or ion cores) and Hartree potential, Σ is the self-energy operator, and $\Psi_{n\mathbf{k}}$ and $\epsilon_{n\mathbf{k}}^{\text{qp}}$ are the quasiparticle wave function and energy. Most quasiparticle calculations use Hedin's *GW* approximation,³

which includes only the lowest-order term in an expansion for the electron self-energy operator

$$\Sigma(\mathbf{r}, \mathbf{r}'; E) + i \int \frac{d\omega}{2\pi} e^{+i\eta\omega} G(\mathbf{r}, \mathbf{r}'; E + \omega) W(\mathbf{r}, \mathbf{r}'; \omega) + \dots$$

For this expansion involving the electron propagator G and screened interaction W , the LDA G and random-phase approximation W can now be used routinely to compute Σ .^{5,6}

Instead of Dyson's equation, methods such as the LDA use the Kohn-Sham equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \Psi_{n\mathbf{k}}(\mathbf{r}) = \epsilon_{n\mathbf{k}}^{\text{KS}} \Psi_{n\mathbf{k}}(\mathbf{r}),$$

where V_{xc} is the "exchange-correlation" potential. The replacement $\Sigma \rightarrow V_{\text{xc}}$ leads to systematic problems with interpreting Kohn-Sham eigenvalues as quasiparticle energies. Most notably, LDA band gaps in nonmetals are too small compared to experiment.⁴⁻⁶ Also, occupied bandwidths of simple metals (e.g., Na) are too large when computed in the LDA,⁷ whereas the bandwidths of interest here tend to be too small.^{5(b),5(c),8} Fortunately, *GW* results agree much more closely with measured gaps and widths.

A typical property of a wide-gap insulator that is influenced by quasiparticle energies is the low-energy (band-gap region) absorption spectrum. A key parameter of influence, the band gap, is affected by up to ~5 eV depending on the theory used.⁸ Much progress is made when studying optical properties of solids by rigidly shifting the energies of all unoccupied states to achieve the correct band gap.⁹ However,

TABLE I. Information affecting pseudopotential construction and band calculations is presented. Pseudopotential information is presented for each element with the first listed material containing it. The reference electronic configuration is presented in the second column. In the third column, pseudopotential cutoff radius r_c and the parameter a_c are presented in ordered pairs in the sequence of states listed in the reference configuration. [As a minor adaptation of the pseudopotential generation scheme, a_c replaces the constant 1.5 found in Eq. (7') of Ref. 19.] An asterisk denotes the angular-momentum channel taken as local. A dagger denotes semilocal pseudopotentials used. The noble-gas-like core used in pseudopotential generation is indicated in square brackets, followed by the core polarizability and s, p , and d CPP parameters (Ref. 21). Plane-wave cutoff energies for electron wave functions, the number of conduction bands and cutoff wave vectors for the bare (G_1) and screened (G_2) Coulomb interaction used in the quasiparticle calculations, and the face-centered-cubic (fcc) lattice constant are also indicated.

Solid	Reference configuration	Pseudopotential/core-polarization parameters		E_{PW} (Ry)	No. of conduction bands used	G_1, G_2 (bohr $^{-1}$)	fcc lattice constant a (Å)
		{ $(r_c$ (bohrs), a_c (bohrs))},	[core], CPP α (bohrs 3), s, p, d r_c (bohr)				
LiD	Li: $s^{0.5}p^{0.2}d^{0.2}$ D: s^0	(1.1,1.5), (1.0,1.5), (2.0,1.8)* [He] 0.1907, 0.9152, 0.8446, 0.8446 (0.2,1.5)* no core		100	60	10,6	7.67
LiF	Li: see LiD F: $s^{1.5}p^{4.25}d^{0.25}$	(0.8,1.5), (0.8,1.5), (1.2,1.8)* [He] 0.0016, 0.2478, 0.2461, 0.2651		100	60	10,6	4.020
LiCl	Li: see LiD Cl: $s^{1.5}p^{4.5}d^{0.5}$	(1.0,1.5),* (1.0,1.5), (1.1,1.5) [Ne] 0.0508, 0.4369, 0.4247, 0.5111 (0.7,1.5), (0.7,1.5)*		36	90	8,5	5.133
C $_{60}$ [†]	C: s^0p^0	[He] 0.0089, 0.4012, 0.3831 (1.4,1.5) (1.4,1.5), (1.4,1.8)*		48	600	10,3	14.26
MgO	Mg: $s^0p^0d^0$ O: $s^{1.5}p^{3.25}d^{0.25}$	[Ne] 0.4777, 0.8172, 0.8715, 0.9580 (0.8,1.5), (0.8,1.5), (1.1,1.8)* [He] 0.0026, 0.2841, 0.2790, 0.3065 (0.95,1.5),* (0.95,1.5), (1.05,1.5)		81	75	8,3.9	4.212
Ar	Ar: $s^{1.5}p^{5.5}d^{0.5}$	[Ne] 0.0370, 0.4011, 0.3877, 0.4683 (1.0,1.5),* (1.0,1.5), (0.8,1.8) [Ne] no core polarization considered		49	95	8,5	5.260
KCl	K: $s^2p^6d^0$	[Ar] 3.3102, 1.2400, 1.2715, 1.3370		36	150	8,5	6.293
CaF $_2$	Cl: see LiCl Ca: $s^0p^0d^0$ F: see LiF	(1.7,1.5),* (1.9,1.5), (1.4,1.5) [Ar] 3.3102, 1.2400, 1.2715, 1.3370		100	90	8,5	5.464

further corrections of a band structure can include a relatively uniform stretching of the individual band complexes. These subtler aspects are difficult to establish experimentally, but have been definitively realized in LiF.⁸ Band dispersion strongly influences absorption features arising from critical points in semiconductors¹⁰ and band dispersion plays a lesser, analogous role in ionic and molecular solids. Excitonic effects relegate the underlying the band structure to being one of several relevant factors influencing the solids' properties.¹¹

This work analyzes self-energy effects on bandwidths in LiD, LiF, LiCl, solid C $_{60}$ (fullerite), MgO (periclase), Ar, KCl (sylvite), and CaF $_2$ (fluorite). For LiD, KCl, Ar, and CaF $_2$, this appears to have required carrying out the most thorough quasiparticle calculations to date. For solids studied, LDA bandwidths are smaller than GW ones and available experiment. Self-energy effects typically compress bands, but the LDA V_{xc} compresses them the most. Compression results from exchange and correlation being stronger on atomic or molecular sites because higher-lying states in a band tend to have more nodes between sites and so are more concentrated on the sites (a consequence of wave func-

tion normalization). Below, the methods used here are presented, as are the results and subsequent discussion, which address the potential relevance of this work to related topics in electronic structures.

METHODOLOGY

LDA and GW effects on bandwidths were found using pseudopotential, plane-wave calculations. Results for C $_{60}$ (Ref. 12) and LiF (Ref. 8) were reported previously, but not as fully regarding bandwidths. Quasiparticle energies have also been found for LiD,¹³ Ar,¹⁴ and KCl,¹⁵ but LiCl [Refs. 5(b) and 5(c)] and MgO (Ref. 16) may be the only systems previously studied in comparable detail at the GW level. Except for C $_{60}$, all results were newly recomputed. This work used separable¹⁷ Hamann-Schlüter-Chiang¹⁸ norm-conserving pseudopotentials with Vanderbilt cutoff functions¹⁹ and with the core-polarization-potential (CPP) approach²⁰ to treat core-valence interactions.²¹ Separable pseudopotentials were tested as in Ref. 8. Experimental crystal structures were assumed and $2 \times 2 \times 2$ or better zone sampling²² was used to obtain self-consistent LDA charge densities. The Ceperley-Alder correlation²³ parametrized by

TABLE II. For the bands studied, bandwidths and gaps as found in the LDA, *GW* approximation, and the Hartree-Fock approximation and available measurements, as well as calculated and measured ϵ_∞ . Because C_{60} was studied in the hypothetical *Fm3* structure, no experimental numbers are provided.

Solid, band	Bandwidth (eV)				Band gap (eV)				ϵ_∞	
	LDA	<i>GW</i>	HF	Expt. ^a	LDA	<i>GW</i>	HF	Expt. ^b	Calc.	Expt. ^c
LiD, D 1s	5.50	5.83	7.57	6.3 ± 1.1 6.0 ± 1.5	2.84	5.37	10.07	5.04	3.59	3.61
LiF, F 2p	3.12	3.61	3.31	3.5(2)	8.82	14.30	21.29	14.2(2)	1.99	1.92
LiCl, Cl 3p	2.99	3.27	3.75		5.90	9.20	14.47	9.4(1)	2.86	2.78
C_{60} , H_u	0.66	0.89	1.06							
C_{60} , T_{1u}	0.52	0.69	0.91		1.04	2.15	5.36			
C_{60} , T_{1g}	0.59	0.78	1.00							
MgO, O 2p	4.73	5.36	5.56		4.75	7.81	14.4	7.83	3.03	2.95
Ar, Ar 3p	1.42	1.59	1.67		8.09	13.62	17.70	14.19	1.71	1.66
KCl, Cl 3p	1.16	1.20	1.22		4.59	8.38	12.12	8.69	2.29	2.19
CaF ₂ , F 2p	2.96	3.49	3.05		6.77	11.38	17.57	11.8	2.12	2.04

^aReference 30.

^bReference 31.

^cReference 32.

Perdew and Zunger²⁴ was employed. *GW* calculations followed the Hybertsen-Louie method⁵ using $4 \times 4 \times 4$ zone sampling. All results are well converged with respect to numerical cutoffs. Relevant numerical parameters are presented in Table I.

Neglecting contributions from exchange and correlation, band energies exemplify the Hartree approximation, which leads to bandwidths that are too large. Because various approximations treat exchange and correlation differently, the electron states' Schrödinger-like equations and wave functions depend on the approximation. As a simplification, this work uses LDA wave functions and expectation values of V_{xc} or self-energy operators to assess effects of an approximation on band energies. Band energies and self-energy contributions were referenced to a band maximum and accompanying self-energy contributions. The relative LDA exchange-correlation contribution to a band energy is

$$\Delta_{nk}^{LDA} = \langle \Psi_{nk} | V_{xc} | \Psi_{nk} \rangle - \langle \Psi_{BM} | V_{xc} | \Psi_{BM} \rangle$$

and the analogous quasiparticle self-energy contribution is

$$\Delta_{nk}^{qp} = \langle \Psi_{nk} | \Sigma(\epsilon_{nk}^{qp}) | \Psi_{nk} \rangle - \langle \Psi_{BM} | \Sigma(\epsilon_{BM}^{qp}) | \Psi_{BM} \rangle.$$

This work's attention to Σ 's energy dependence is important. As expected and confirmed, neglecting this dependence exaggerates widths by a factor $\approx (1 + \langle \partial \Sigma(\epsilon) / \partial \epsilon \rangle)^{-1}$, where the derivative is one typical for the band states. Such neglect greatly exaggerates differences between LDA and *GW* results. Analogous Hartree-Fock (HF) results are obtained using

$$\Delta_{nk}^{HF} = \langle \Psi_{nk} | \Sigma^{HF} | \Psi_{nk} \rangle - \langle \Psi_{BM} | \Sigma^{HF} | \Psi_{BM} \rangle.$$

Like the LDA and *GW* approximation, the HF approximation usually introduces a contribution that reduces bandwidths.

RESULTS AND DISCUSSION

Table II shows bandwidths and gaps and the random-phase approximation dielectric constant ϵ_∞ (obtained with the LDA *G*). The trends for *GW* gaps and ϵ_∞ are noted, while LDA widths are smaller than *GW* and HF ones. Available

experiment results are also given. Figure 1 demonstrates band compression in the LDA and *GW* approximation by showing Δ_{nk}^{qp} and Δ_{nk}^{LDA} vs the LDA band energy. Results are shown for the highest occupied bands and the lowest two unoccupied complexes in C_{60} . The effects on the bandwidths of exchange and correlation are presented in Table III, as found in the LDA, the *GW* approximation, and the HF approximation (which has exchange only). Regarding scatter in the results for C_{60} , the correspondence of the LDA and *GW* results in Fig. 1 suggests that this scatter is not the result of poor numerical convergence.

Trends in bandwidths are clearly established and, because solids are grouped by the pertinent element in Table III, distinctions of the elements are also evident. Results have also been presented for graphite²⁵ and diamond,²⁶ for both of which the HF approximation and the LDA respectively exaggerate and underestimate the (occupied) valence band width, and the *GW* approximation has yielded bandwidths in

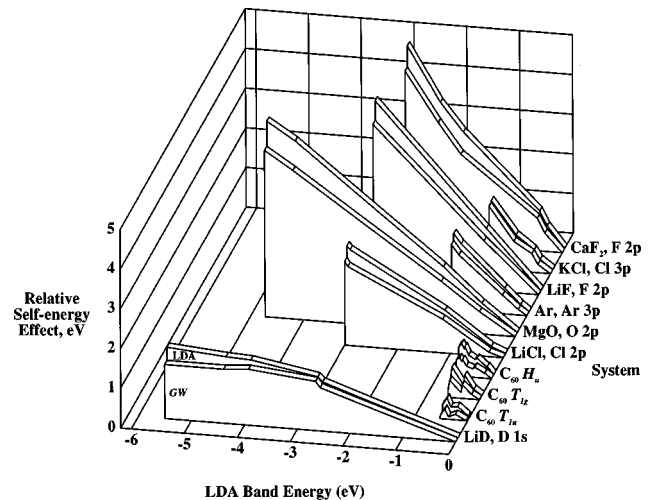


FIG. 1. Relative contributions to band energies Δ_{nk}^{LDA} , labeled “LDA,” and Δ_{nk}^{qp} , labeled “*GW*,” vs the LDA band energy, for the bands studied. Contributions are defined as zero for states at the valence-band maximum.

TABLE III. For the bands studied, effects on widths because of the LDA V_{xc} , Hartree-Fock Σ^{HF} , GW correlation ($\Sigma - \Sigma^{HF}$), and GW (Σ). All units are eV.

Solid, band	V_{xc}	Effects on bandwidth (eV)		
		Σ^{HF}	$\Sigma - \Sigma^{HF}$	Σ
LiD, D 1s	-1.69	0.38	-1.74	-1.36
C ₆₀ , H_u	-0.63	-0.23	-0.17	-0.40
C ₆₀ , T_{1u}	-0.25	0.14	-0.22	-0.08
C ₆₀ , T_{1g}	-0.40	0.01	-0.22	-0.21
MgO, O 2p	-4.83	-4.00	-0.20	-4.20
LiF, F 2p	-4.46	-4.27	0.30	-3.97
CaF ₂ , F 2p	-4.80	-4.71	0.44	-4.27
LiCl, Cl 3p	-2.40	-1.64	-0.48	-2.12
KCl, Cl 3p	-1.62	-1.56	-0.02	-1.58
Ar, Ar 3p	-1.82	-1.57	-0.08	-1.65

close agreement with experiment. Many-body effects on bandwidths differ from those in the solids of interest here, including C₆₀, because C 2s and C 2p states are respectively weighted most heavily at the bottom and top of the valence bands. Influences beyond the role played by the bonding vs antibonding character of the band states may therefore also arise. Exchange alone gives a substantial positive contribution to the bandwidth in both systems (≈ 12 eV in graphite and ≈ 5 eV in diamond).

Further influences of electron-electron interactions and vibrational (polaronic) corrections to band energies could also be relevant. The effects of terms beyond the GW approxima-

tion in insulators have been considered²⁷ and consequences of the transfer of spectral weight from quasiparticle peaks to satellites remain to be examined. Polaronic corrections seem yet to be treated within a realistic description of solids. Hints of the relevance of such corrections are those anticipated for conduction bands in alkali halides²⁸ (which could affect the band gap) and the 0.1-eV difference in band gaps of LiH and LiD.²⁹ Tests show that this difference does not result from the different lattice constants, but, because of the smaller gap in LiH, polaronic effects should move the present, frozen-lattice GW gap in the right direction.

CONCLUSIONS

This work has compared the LDA and GW results for electron bandwidths in eight ionic, noble gas, or molecular solids. The bands considered are those derived from degenerate atomic or molecular levels, e.g., F 2p in LiF or the H_u states in C₆₀. Both the LDA and the GW approximation indicate compression of bands by exchange and correlation. However, the LDA leads to the narrowest bands and, where detailed comparison can be made, the GW results are closer to experiment. This occurs because exchange and correlation are strongest on atomic or molecular sites, while states at the tops of bands typically have more nodes between such sites and are therefore more concentrated on the sites. The similarity of the LDA and GW exchange-correlation effects on band dispersion is remarkable. Other physical effects (polaronic, in particular) have been noted and attention to them would be timely.

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eV is the indirect gap inferred from the 12.1-eV direct gap proposed by G. W. Rubloff, Phys. Rev. B **5**, 662 (1972).

³²For LiD, I follow Ref. 13; for LiF, MgO, and CaF₂, ϵ_∞ was estimated as $n^2(0.76\lambda_0)$, where λ_0 is the zero-dispersion wavelength ($d^2n/d\lambda^2=0$) and n is the index of refraction. Optical data used were found in *Handbook of Infrared Optical Materials*, edited by P. Klocek (Marcel Dekker, New York, 1991). For LiCl and KCl see R. S. Knox and K. J. Teegarden, *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), p. 625; for Ar see A. C. Sinnock and B. L. Smith, Phys. Rev. **181**, 1297 (1969).