RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

Electron correlation and the band gap in ionic crystals

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(Received 16 September 1985)

The band gap and quasiparticle energies in LiCl are calculated by evaluation of the electron self-energy operator including the effects of local fields and dynamic screening from first principles. Good agreement with available experimental data is obtained. In particular, the calculated band gap for bulk transitions (8.9 eV) is within 5% of the experimental result. Comparison with our previous study of homopolar materials shows that the same theoretical picture describes the electron correlation in both cases.

In this paper we extend a theory of the quasiparticle energies in semiconductors and insulators[1] to the case of ionic crystals exemplified by lithium chloride. Although the alkali halides are traditionally viewed as composed of atomiclike ions with spectra dominated by atomic excitations and thus quite different from the homopolar materials, we find that the same theory gives good account of both the valence-band features and the direct gap for bulk transitions in LiCl. In particular, the calculated band gap of 8.9 eV is 3 eV larger than the gap in the density-functional eigenvalues and is within 5% of the value extracted from optical data. As compared to the semiconductors, the same trends are observed. The roles of local field effects (full dielectric matrix) and dynamical effects in the screening are similar and crucial for a quantitative theory.

Inclusion of electronic polarization effects (correlation) in the treatment of alkali halides has a history nearly as long as the treatment of correlation in metals. In particular, Toyozawa introduced the idea of an electronic polaron to describe the polarization of the crystal produced by an extra electron or hole.[2] The model envisions the extra electron causing atomiclike excitations on the halide ions, which in turn react back on the electron giving a correlation contribution to its energy. He formulated this as an effective electron-exciton interaction with a simple model for the coupling constant. Fowler,[3] and later Kunz,[4] developed these ideas further in connection with estimating correlation corrections to the Hartree-Fock band structure in wide-gap insulators. Although physically appealing, these calculations were limited by the simplicity of the model and the necessity of a wave-vector cutoff. Hermanson[5] proposed a similar idea based on work of Overhauser[6] for metals with the excitons replaced by plasmons. There have also been several calculations of the electron self-energy based on the Coulomb-hole–screened-exchange (COHSEX) approximation,[7] an essentially static model. In these cases,[5,7] the off-diagonal elements of the dielectric matrix (local field effects) were further neglected. As we have found,[1] these are quite important for quantitative results for screening in insulators and semiconductors. Finally, we note that the eigenvalues in the local-density-functional[8,9] theory do not give good results for the excitation energies in these materials, although Heaton, Harrison, and Lin[10] and Heaton and Lin[11] have applied a self-interaction correction (SIC) approach to LiCl which seems to give significantly better agreement for the direct gap.

In the present approach, we obtain the quasiparticle energies by solving the equation[12]

$$(T+V_{\mathrm{ext}}+V_H)\psi_{n\mathbf{k}}(\mathbf{r})+\int d\mathbf{r}'\,\Sigma(\mathbf{r},\mathbf{r}';E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')=E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})\;, \tag{1}$$

where V_H is the average (Hartree) Coulomb interaction and the exchange and correlation contributions are included in the nonlocal energy-dependent self-energy operator Σ. In general, Σ as well as $E_{n\mathbf{k}}$ is complex with the imaginary part giving the lifetime of the excitation in the quasiparticle picture. In the present paper, we consider only the real part of Σ. The GW approximation for Σ is used here:[12]

$$\Sigma(\mathbf{r},\mathbf{r}';E)=i\int(d\omega/2\pi)e^{-i\delta\omega}G(\mathbf{r},\mathbf{r}';E-\omega)W(\mathbf{r},\mathbf{r}';\omega)\;. \tag{2}$$

δ is a positive infinitesimal. The full interacting Green's function G and the dynamically screened Coulomb interaction, $W=v\epsilon^{-1}$, for the crystal are required inputs. Our approach[1] is to make the best possible approximation for G and W separately, evaluate Σ, and obtain the spectrum.

As described in Ref. 1, the spectrum and wave functions from a density-functional calculation are used for the initial construction of the Green's function. Because the change in the spectrum for a wide-gap insulator is relatively large, it is necessary to iterate once with the new spectrum as described below. The static dielectric matrix $\epsilon_{\mathbf{GG}'}(\mathbf{q};\omega=0)$ can be obtained from first principles within the density-functional formalism.[9] Consistent with our choice of vertex function, $\Gamma=1$, we evaluate the dielectric matrix within the random-phase approximation by use of the Adler-Wiser formulation.[13] To extend the dielectric function to finite frequency, we introduced the generalized plasmon pole approximation in Ref. 1. For each set of momentum components $(\mathbf{q},\mathbf{G},\mathbf{G}')$, $\mathrm{Im}\epsilon^{-1}$ is taken to be

$$\mathrm{Im}\epsilon^{-1}_{\mathbf{GG}'}(\mathbf{q};\omega)=A_{\mathbf{GG}'}(\mathbf{q})[\delta(\omega-\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q}))-\delta(\omega+\tilde{\omega}_{\mathbf{GG}'}(\mathbf{q}))]\;. \tag{3}$$

The full ω-dependent dielectric matrix can then be obtained once the matrices A and $\tilde{\omega}$ are determined by use of two sum rules that insure each component has the exact ω and ω^{-1} moments. This requires only the *ab initio* static dielectric matrix and the valence charge density and depends on no adjustable parameters.[1]

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The frequency integral in Eq. (2) can then be done straightforwardly. To solve Eq. (1), we expand the quasiparticle wave function $\psi_{n\mathbf{k}}$ in terms of the local-density-approximation (LDA) wave functions $\phi_{n\mathbf{k}}$. The underlying density-functional calculations are done with use of the LDA (Ref. 14) with the pseudopotential approach[15] and a plane-wave expansion for the wave functions. In particular, this implies that the core-valence interaction together with core-polarization terms are assumed to be approximated by the core-valence interaction built into the pseudopotential. As these terms are small,[12] this should be reasonable. A 25-Ry cutoff in the plane-wave energy is used in the expansion of the LDA wave functions. The dielectric matrices employed are approximately 220×220 depending on $\mathbf{q}$. The resulting macroscopic dielectric constant is calculated to be 3.3 as compared to the experimental electronic contribution of 2.7, showing the same trend as for the homopolar semiconductors. We have found by direct diagonalization of Eq. (1) that the quasiparticle wave function has 99.9% overlap with the corresponding LDA wave function. Therefore, only diagonal matrix elements $\langle\phi_{n\mathbf{k}}|\Sigma|\phi_{n\mathbf{k}}\rangle$ need be considered for the following discussion. Finally, the self-energy operator in (1) must be evaluated at the quasiparticle energy $E_{n\mathbf{k}}$.

The quasiparticle energies obtained as described are significantly different from the LDA eigenvalues. To get further insight, we plot the change from the LDA spectrum versus the quasiparticle energies in Fig. 1. We observe that the change is dominated by a large rigid downward shift of 2 eV for the valence bands and an upward shift of 1 eV for the conduction bands. There is a small slope in addition, as well as some scatter. The straight lines are drawn to guide the eye and illustrate this point. Thus the changes in the band dispersion are small but the gap is significantly larger. The results illustrated in Fig. 1 are also contrary to the assumption made by Heaton, Harrison, and Lin[10] and Heaton and Lin[11] in applying a self-interaction correction to the LDA: The changes in the conduction band are nonzero and represent approximately one-third of the correction to the gap.

Because of these relatively large changes, our use of the LDA spectrum in G must be checked. We have iterated once incorporating the changes in the spectrum indicated by Fig. 1. This causes only a small further change for the spectrum: the Cl 3s band is shifted downward by an additional 0.4 eV, the Cl 3p band is essentially unchanged, and the gap is further opened up by 0.2 eV. These changes are sufficiently small compared to the original shifts to indicate that there is no further need to iterate. The results reported here incorporate these self-consistency effects. Also, because of the finite size of the dielectric matrices employed, we estimate the direct gap to have converged to within 0.3 eV and the relative intraband energies to within 0.1 eV.

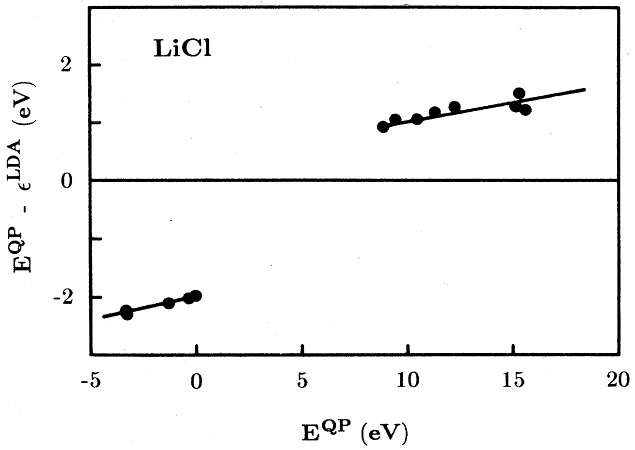

FIG. 1. Plot of the change in the quasiparticle energy (E^{QP}) from the density functional energy (ϵ^{LDA}) vs the quasiparticle energy. The zero of energy is taken at the valence-band edge. The straight lines are drawn as guides to the eye.

In Table I, we summarize the available experimental data[16–21] for LiCl as well as other available theoretical calculations.[10,11,22] Comparison of the conduction-band states to optical experiments is complicated by the strong excitonic effects in the spectra. The conduction-band edge for bulk transitions is estimated to be at approximately 9.4 eV above the valence-band edge,[16] although experimental assignment is uncertain because the onset of bulk transitions is obscured. Also, the finite size of the dielectric matrices noted above leads to a slight underestimate of the theoretical gap. In view of this, the calculated result for the gap, 8.9 eV, agrees well with the experiment. As is well known, the Hartree-Fock result is too large, although estimates of the polarization effect plus local relaxation around the hole yield better results.[22] We note that the SIC approach shows significant scatter in the calculated gap depending on the electron-gas data employed.[11]

We find that the center of the Cl 3s band is located 11.5 eV below the centroid of the Cl 3p band, in good agreement

TABLE I. Comparison of results (in eV) from the present calculation of the quasiparticle energies to the results from the LDA eigenvalues, experiment, and other calculations discussed in the text. Results are shown for the band gap E_g, Cl 3p bandwidth W_{3p}, and separation between the Cl 3s and 3p bands $E_{3p}-E_{3s}$.

	LDA	SIC[a]	HF[b]	pol[b]	Present work	Expt.
E_g	6.0	9.9–10.6	16.9	9.7	8.9	9.4[c]
W_{3p}	3.5	2.9	4.6	3.6	3.8	4.0 ± 0.2[d]
$E_{3p}-E_{3s}$	11.3	12.6	· · ·	· · ·	11.5	11.6 ± 0.5[e], 11.0 ± 0.6[f]

[a] Reference 11.
[b] Reference 22.
[c] Reference 16.
[d] Reference 19.
[e] Reference 17.
[f] Reference 18.

with our estimate of the separation between the 3s and 3p peaks in the x-ray photoemission experiment of Ref. 17 as well as the data from electron spectroscopy for chemical analysis from Ref. 18. To compare our Cl 3p bands meaningfully to the uv photoemission data of Poole, Jenkin, Leckey, and Liesegang[19] and Poole, Jenkin, Liesegang, and Leckey,[20] we have done a p-band Slater-Köster least-squares fit to our results at eight points in the irreducible part of the Brillouin zone. (The rms fit error is 0.07 eV.) The density of states was then generated from the tight-binding bands and broadened with a Gaussian of full width at half maximum of 0.3 eV suggested by the experimental resolution cited in Ref. 20. The resulting density of states is displayed in Fig. 2 together with the data of Poole *et al.*,[20] showing excellent overall agreement. We estimate the bandwidth with respect to the background indicated in Fig. 2 to be approximately 4 eV as reported in Ref. 19. The theoretical width of the spectrum is approximately 0.2 eV narrower than the experimental spectrum, or less, depending on precisely what experimental resolutions were to be incorporated. (The resolution quoted in Ref. 19 is 0.75 eV.) We also note that the separation between the peaks in Fig. 2 (2.0 eV) agrees well with the uv spectra of Pong and Smith[21] (1.8 ± 0.4 eV). For comparison, the Hartree-Fock (HF) calculation gives too large a bandwidth with the polarization corrections (pol) improving the agreement.[22] The self-interaction correction results in a slightly narrower bandwidth than the LDA, which is already too narrow.[11] (Note that the HF, HF with polarization, and SIC results are unbroadened.)

In Table II, the results are presented for successively better approximations to the self-energy with more physical input included at each step:[1] the COHSEX approximation with no local fields, the COHSEX approximation with local fields (the full static dielectric matrix), and the GW approximation. The trend is exactly the same as observed for the homopolar semiconductors.[1] Correct treatment of the crystalline Green's function (nonlocality) improves the gap as compared to the LDA. Inclusion of local field effects dramatically increases the gap because the screening at points of high charge density (halide sites) is appropriately more effective than at points of low charge density (alkali sites). Finally, if we envision a correlation as arising from virtual emission and reabsorption of plasmons (as discussed further below), the COHSEX (static) approximation overestimates the energy denominator for that process. Dynamic screening in the GW formulation is essentially the same as a proper account of the energy denominator and is required for a quantitative account of correlation.

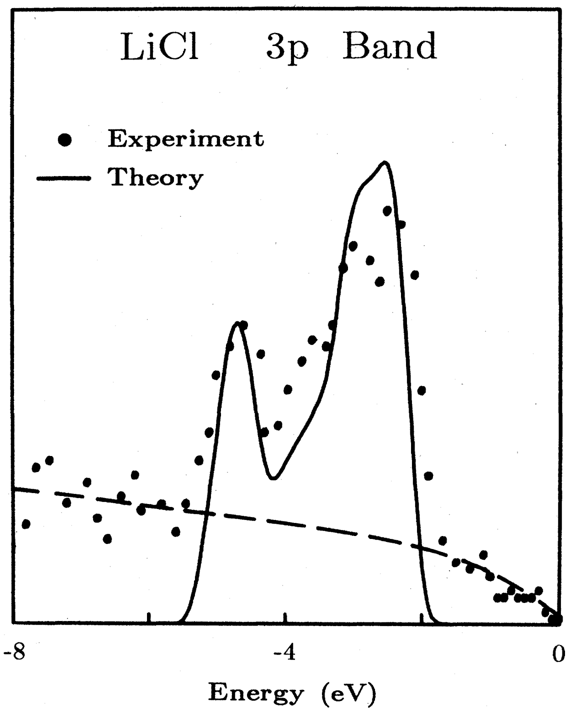

FIG. 2. Plot of the theoretical density of states described in the text compared to the photoemission spectrum from Ref. 20. The zero of energy is arbitrary and the density of states has been scaled. The dashed line represents the approximate background in the experimental data.

The generalized plasmon pole model described by Eq. (3) can be shown to be equivalent to the plasmon-electron coupling model of Overhauser,[6] appropriately generalized to include interband scattering and the effect of periodicity leading to a plasmon band structure.[23] As emphasized by Overhauser, the effective excitation $\tilde{\omega}_p$ is only a true plasmon for small q. For $\mathbf{G},\mathbf{G}'$ nonzero, it is an effective mode representing coupling to the electron-hole continuum. This must be essentially free-electron-like for large $\mathbf{G},\mathbf{G}'$ and, for the off-diagonal case, represents the mode with the largest coupling to charge fluctuations of wave vector $\mathbf{q}+\mathbf{G}$ and $\mathbf{q}+\mathbf{G}'$. We note that because of the quantitative importance of umklapp scattering ($\mathbf{G},\mathbf{G}'\neq 0$), virtual electron-hole creation is not negligible. However, dressing of the bare excitations by virtual emission and reabsorption of

TABLE II. Comparison of results (in electron volts) by use of the COHSEX approximation with no local fields, with local fields, and the GW approximation with local fields to the results from the LDA eigenvaues and experiment. Notations are as in Table I.

	LDA	COHSEX no LF	COHSEX LF	GW	Expt.
E_g	6.0	8.2	10.4	8.9	9.4[a]
W_{3p}	3.5	4.2	3.5	3.8	4.0 ± 0.2[b]
$E_{3p}-E_{3s}$	11.3	13.6	12.6	11.5	11.6 ± 0.5[c], 11.0 ± 0.6[d]

[a] Reference 16.
[b] Reference 19.
[c] Reference 17.
[d] Reference 18.

plasmons is clearly important.

In conclusion, we have shown that our theory of the quasiparticle energies in semiconductors and insulators extends to the case of ionic crystals. Despite the qualitatively different character of binding in alkali halide crystals as compared to homopolar semiconductors, a single theoretical picture emerges which can describe the excitation energies in both cases. Microscopically, this is possible because the inclusion of local field effects in the dielectric screening allows the screened Coulomb interaction to reflect the strong inhomogeneity in the charge density of the crystal. This is true whether the inhomogeneity is due to strong ionicity or covalent bonding.

This work was supported by National Science Foundation Grant No. DMR8319024. The work was facilitated by the IBM Distributed Academic Computing Environment at the University of California at Berkeley. One of us (M.S.H.) gratefully acknowledges the financial support of IBM during the early phases of this work.

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