Theory of Quasiparticle Energies in Alkali Metals

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The quasiparticle band structures of Na and Li are calculated by evaluation of the electron self-energy to first order in the dynamically screened Coulomb interaction. For Na, our results explain quantitatively the large bandwidth reduction observed in recent angle-resolved photoemission experiments. The inclusion of exchange-correlation effects in the dielectric screening and the requirement that the energy dependence of the electron Green's function be treated self-consistently are found to be important in our obtaining the correct bandwidths.

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The early work of Hedin[1] and Lundqvist[2] suggested that electronic correlation effects reduce the occupied electron energy bandwidth by 5% to 10% relative to the free-electron value in a low-density homogeneous electron gas. Recently, however, Jensen and Plummer[3] reported photoemission results for Na which indicate a 25% smaller bandwidth than that expected on the basis of free-electron or density-functional band-structure calculations. While both local-density-functional (LDA) and free-electron calculations give a bandwidth near 3.2 eV for Na, the photoemission results indicate an occupied valence bandwidth of only 2.5 eV. These results imply that the many-body self-energy correction to the bandwidth is 0.7 eV. However, the previous self-energy calculations predict[1,2] at most a 0.3-eV narrowing. This apparent disagreement between experiment and theory has stimulated new theoretical work on possible additional correlation mechanisms,[4,5] as well as a more sophisticated interpretation of the photoemission data.[6]

In this Letter, we show that excellent agreement with experiment can be achieved with improved self-energy calculations. Following Hedin,[1] we employ the GW approximation wherein the electron self-energy is given by the first term in an infinite series containing successively higher powers of the dynamically screened Coulomb interaction. In his calculations, Hedin employed the free-electron Green's function and used the Lindhard (i.e., RPA with no exchange-correlation effects) dielectric function for the electron gas to screen the Coulomb interaction. The present calculation is different in several respects. We have included the effects of exchange and correlation in the dielectric function as they enter it in (local) density-functional theory. We also require that the energy dependence of the electron Green's function be consistent with the calculated quasiparticle spectrum. The effects of local fields in screening and the crystalline Green's function are also included. By employing the LDA dielectric function and enforcing the self-consistency requirement, we obtain a self-energy correction to the LDA bandwidth of 0.7 eV for both Na and Li. This is a significantly larger correction than those obtained previously and results in a Na occupied bandwidth of 2.5 eV. This result is in excellent agreement with experiment.

The quasiparticle spectrum, $E_{n\mathbf{k}}$, is determined by solving a Dyson equation

$$(T+V)\psi_{n\mathbf{k}}(\mathbf{r})+\int\Sigma(\mathbf{r},\mathbf{r}',E_{n\mathbf{k}})\psi_{n\mathbf{k}}(\mathbf{r}')d^3r' = E_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r}). \quad (1)$$

Here, $V=V_{\text{ext}}+V_{\text{H}}$ with V_{ext} the external potential and V_{H} the Hartree term, and Σ is the self-energy operator. Σ includes the effects of exchange and correlation among the valence electrons[7] and may be written exactly in the following form[1]:

$$\Sigma(12)=i\int W(13)G(14)\Gamma(423)d(34), \quad (2)$$

where an abbreviated notation in which $(1)=(\mathbf{r},\sigma,t)$ is employed. G is the Green's function for the valence electrons, and W is the screened Coulomb interaction. Here, W is given by

$$W(12)=\int v(13)[\delta V(2)/\delta V_{\text{ext}}(3)]d(3), \quad (3)$$

where v is the bare Coulomb interaction. W can be calculated directly if the inverse dielectric function for a test charge, $\epsilon^{-1}(12)=\delta V(1)/\delta V_{\text{ext}}(2)$, is known. The corresponding vertex function is given by

$$\Gamma(123)=\delta(12)\delta(13)+\delta\Sigma(12)/\delta V(3). \quad (4)$$

An exact solution of these coupled equations for Σ, W, G, and Γ is not feasible. We approximate $\Sigma(12)=iG(12)W(1^+2)$, the GW approximation, and proceed to calculate G and W as accurately as possible. This ap-

proach has been taken previously with success in the calculation of the quasiparticle band structures of semiconductors and insulators.[8] The precise role of vertex corrections (higher-order terms in the perturbation series in W) is not clear even for the electron gas, and estimates of their importance vary considerably.[4,5,9] Minnhagen's evaluation of the spectral function to second order in W indicates that the *position* of the quasiparticle peaks does not shift significantly when the high-order terms are included.[10]

We use a quasiparticle approximation for the Green's function

$$G(\mathbf{r},\mathbf{r}',\omega)=\sum_{n,\mathbf{k}}\frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi^*_{n\mathbf{k}}(\mathbf{r}')}{\omega-E_{n\mathbf{k}}-i\delta\,\mathrm{sgn}(E_F-E_{n\mathbf{k}})}, \quad (5)$$

where ψ and E are quasiparticle wave functions and energies from Eq. (1). Initially, we construct G from the LDA eigenvalues and eigenfunctions obtained from solutions to the Kohn-Sham[11,12] equations. Subsequently, we replace the LDA energy spectrum with the quasiparticle spectrum which must, therefore, be determined self-consistently. The LDA eigenfunctions, obtained from a first-principles pseudopotential calculation in a plane-wave basis, are used throughout the calculation.

In principle, the screened interaction depends on the vertex function, so there is an apparent ambiguity concerning the proper W to be used in conjunction with the GW approximation. Fortunately, W can be calculated without explicit knowledge of the vertex function if the screening properties of the system embodied in the dielectric function are known. We obtain the dielectric function through the use of density-functional theory and the generalized plasmon-pole model.[8] We note, as pointed out by Strinati, Mattausch, and Hanke,[13] that within the GW approximation explicit inclusion of exchange-correlation effects in W beyond the RPA leads to better satisfaction of the Ward identity associated with particle conservation.

The calculation of the dynamically screened Coulomb interaction, therefore, requires the appropriate frequency-dependent dielectric function. To obtain it, we calculate the static dielectric matrix, including local fields, as it is given by density-functional theory and then extend to finite frequencies with use of a generalized plasmon-pole model.[8] Evaluation of the functional derivative in the definition of W in Eq. (3) by use of the density-functional approach gives

$$\epsilon^{-1}=1+v[1-x_0(v+K_{xc})]^{-1}\chi_0, \quad (6)$$

where $K_{xc}=\delta V_{xc}/\delta\rho$, and χ_0 is the independent-particle polarizability. V_{xc} is the exchange-correlation potential in the density-functional theory. The static dielectric function is a ground-state property of the system and could be calculated exactly if the correct K_{xc} were known. In our work, we have calculated K_{xc} in the LDA.[14] Note that the usual RPA dielectric function is obtained by dropping K_{xc} in Eq. (6).

In Fig. 1, we compare the calculated quasiparticle energies for Na with the experimental dispersion and with the LDA eigenvalues. Overall the calculated quasiparticle dispersion has the correct shape and magnitude in relation to experiment. The origin of the cluster of experimental points near E_F is still under debate. Extra peaks in the intensity can arise because the normal component of the electron wave vector is not conserved in the photoemission process.[6] Alternatively, Overhauser has argued that the extra peak is indicative of a charge-density wave in Na.[15]

The calculated quasiparticle bandwidth for the occupied states for Li is 2.75 eV. This result is similar to Na: It also corresponds to a 0.7-eV reduction relative to the LDA value. There is at present no experimental dispersion relation available for Li. However, soft-x-ray data[16] suggest an occupied valence bandwidth of 3.0 $\pm$0.1 eV.

In Fig. 2, we show the calculated self-energy correction ($\Delta=E_{QP}-E_{LDA}$) to the LDA eigenvalues as a function of k for Na. With use of the LDA spectrum and the LDA dielectric matrix, we obtain an occupied-bandwidth reduction of 0.57 eV. Self-consistent inclusion of the quasiparticle spectrum in G in Eq. (5) leads to a further reduction in the bandwidth. The final self-consistent quasiparticle bandwidth is reduced from that of the LDA calculation by 0.71 eV. This value has an estimated numerical uncertainty of $\pm$0.1 eV. As a comparison, with the RPA dielectric function in W and the LDA eigenvalue spectrum in G, one obtains a bandwidth reduction of only 0.31 eV. This reduction is close to Hedin's electron-gas result of 0.27 eV. The approximate equality of these two stems from the similarity between the calculated Na RPA dielectric function and the Lindhard result for the electron gas and the similarity between the LDA energy spectrum and the free-electron

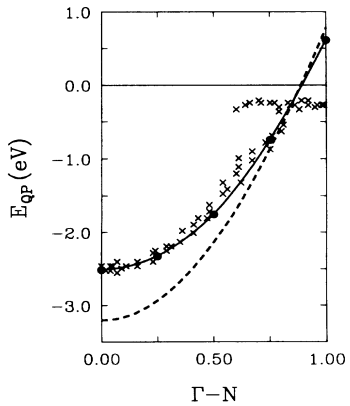

FIG. 1. Quasiparticle energies for Na: Experimental data from Ref. 3 (crosses), LDA eigenvalues (dashed line), and calculated quasiparticle energies (filled circles).

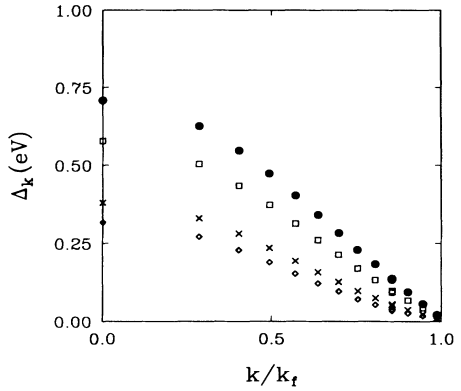

FIG. 2. Self-energy correction to the LDA eigenvalues for states in the first band of Na. Results are obtained with four different methods of evaluating Σ: Non-self-consistent RPA (lozenges), self-consistent RPA (crosses), non-self-consistent LDA (open squares), and self-consistent LDA (filled circles). See text.

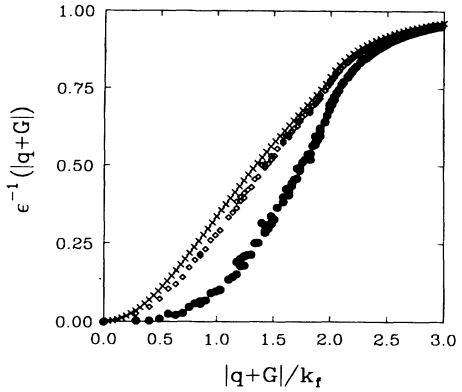

FIG. 3. Diagonal elements of the inverse dielectric matrix for Li: Lindhard formula with $r_s = 3.25$ (crosses), calculated RPA dielectric matrix (lozenges), and calculated LDA dielectric matrix (filled circles).

spectrum.[17] Replacing the LDA spectrum with the calculated quasiparticle spectrum leads to a further reduction in the bandwidth of 0.06 eV. However, the total reduction obtained when exchange-correlation effects in the screening are neglected is only about $\frac{1}{2}$ as large as needed to account for the observed bandwidth.

In our analysis, we find that local-field effects which are described by the off-diagonal elements of the dielectric matrix do not significantly affect the value of the bandwidth for alkali metals. This is in contrast to the important role they play in the band gaps of semiconductors and insulators.[8] On the other hand, inclusion of exchange and correlation effects in the dielectric screening is relatively more important for the alkali metals than for the semiconductors. In Fig. 3, we plot the diagonal elements of the inverse dielectric matrix (IDM) for Li calculated with three different methods. Results for Na are similar. The diagonal elements of the RPA IDM are quite close to the values obtained with the Lindhard expression for the electron gas ($r_s = 3.25$). The difference arises from band-structure effects in Li. The LDA IDM, in contrast, is significantly reduced from the RPA: Exchange and correlation enhance the screening properties of the system.

The larger self-energy correction obtained with the LDA IDM can be traced to the difference between the LDA and RPA dielectric functions. In the present formulation, the self-energy separates into two terms: the screened-exchange term and the Coulomb-hole term. The screened-exchange term corresponds to the usual first-order exchange energy of Hartree-Fock, but with a dynamically screened Coulomb interaction. Within the plasmon-pole model, the Coulomb-hole term may be interpreted as the interaction energy in second-order perturbation theory of an independent electron with the plasmons. One may partially understand the mass enhancement (bandwidth reduction) observed in the alkali metals by analogy to the polaron problem where the mass enhancement is proportional to the electron-phonon coupling strength. In the Coulomb-hole term, the electron-plasmon coupling strength is inversely proportional to the plasmon frequency, and as the IDM determines the q dependence of the plasmon frequency, it also determines the q dependence of the coupling strength. The LDA IDM flattens, relative to the RPA IDM, the dispersion of the plasmon and thereby leads to a stronger electron-plasmon coupling. Thus, the LDA dielectric function gives a larger mass enhancement than that of the RPA. However, we should add that the screened-exchange term also plays a significant role in the bandwidth reduction.

Recently, Zhu and Overhauser[4] and Ng and Singwi[5] have included approximately the effect of interaction with spin fluctuations (paramagnons) in Σ for the case of the electron gas. This effect arises entirely from the vertex function and is therefore sensitive to the approximations used for evaluating Γ. The results of the two calculations differ substantially thus indicating the difficulty in obtaining a reliable approximation for Γ.

In conclusion, we have demonstrated that the inclusion of exchange-correlation effects in the dielectric matrix together with a self-consistent treatment of the energy dependence of the electron Green's function results in a self-energy correction of 0.7 eV to the LDA value of the occupied bandwidth for both Na and Li. These corrections are much larger than those obtained by use of the RPA dielectric function and are in very good agreement with experiment.

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