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Occupied quasiparticle bandwidth of potassium

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The quasiparticle energies and occupied bandwidth of potassium are calculated with a first-principles self-energy approach. The valence-electron self-energy operator is obtained in the *GW* approximation, evaluating the self-energy to first order in the screened Coulomb interaction *W* and the single-particle Green function *G*. Vertex corrections are not included in this approach. We treat the electron-ion interaction with the *ab initio* pseudopotential scheme. The static dielectric screening matrix which includes the effects of exchange and correlation is obtained as a ground-state quantity from a local-density (LDA) calculation, and is extended to finite frequencies by a generalized plasmon-pole model. The electron Green function is obtained in the quasiparticle approximation by use of the self-consistent quasiparticle energies. We find that the calculated occupied bandwidth is reduced from a LDA Kohn-Sham value of 2.27 eV to 1.58±0.1 eV. This result is consistent with existing soft-x-ray emission data. It is also in agreement with a recent photoemission experiment.

I. INTRODUCTION

Local-density-approximation (LDA) calculations have given poor results for the occupied bandwidths of alkali metals,[1,2] owing to the fact that the Kohn-Sham eigenvalues are not strictly related to the single-particle excitation energies. More rigorous calculations of the occupied bandwidth for these systems have been performed by several authors,[2–7] using the electron self-energy operator to obtain the energies of the single-particle excitations. This requires proper treatment of the screened Coulomb interaction and the dressed Green function contained in the self-energy to obtain reasonable results. For example, electron-gas calculations using the random-phase-approximation (RPA) dielectric function for the screening and using the noninteracting Green function result in improvements from the LDA or free-electron bandwidths,[3] but these results still do not agree with photoemission experiments[1] for sodium. Other approaches are more successful.[2,4–7] In particular, an *ab initio* method for calculating the crystalline self-energy operator has been devised[2,8,9] using the self-consistent quasiparticle energy spectrum in the Green function with a dielectric matrix that includes the effects of exchange and correlation on the screening. It has been successful in obtain the occupied bandwidths of lithium and sodium[2] ($r_s=3.24$ and 3.93, respectively), producing a substantial correction from the LDA bandwidth in agreement with experiment.

In the present work, the method is extended to the case of potassium ($r_s=4.86$). The calculated occupied bandwidth for potassium is found to be only 1.58±0.1 eV versus the LDA value of 2.27 eV. Experimental soft-x-ray emission results for this quantity range from 1.26 to 2.2 eV.[10–13] Most recently, an angle-resolved photoemission experiment has found the occupied potassium bandwidth to be 1.4 eV.[7]

II. THEORETICAL METHOD

A. The *GW* approach

The quasiparticle excitations satisfy the Dyson equation in which the energies are given by[3]

$$[T+\phi+v_H]\psi(\mathbf{r})+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E)\psi(\mathbf{r}')=E\psi(\mathbf{r}) \tag{1}$$

where T represents the kinetic energy operator, ϕ the ionic crystal pseudopotential, v_H the Hartree potential, and Σ contains the valence electron-electron exchange and dynamical correlation effects on the energies.

Σ can be obtained formally be a set of coupled functional derivative equations[3] which are

$$\Sigma(1,2)=i\int W(1^+3)G(1,4)\Gamma(423)d(34)\ , \tag{2}$$

$$W(1,2)=v(1,2)+\int W(1,3)P(3,4)v(4,2)d(34)\ , \tag{3}$$

$$P(1,2)=-i\int G(1,3)G(4,1^+)\Gamma(342)d(34)\ , \tag{4}$$

$$\Gamma(123)=\delta(1,2)\delta(2,3)+\int\frac{d\Sigma(1,2)}{dG(4,5)}G(4,6)G(7,5)\Gamma(673)d(4567) \tag{5}$$

where G is the dressed crystalline Green function, v is the Coulomb interaction, Γ is the vertex function, P the polarization propagator, and W the screened Coulomb interaction. The index 1 represents the coordinates $(\mathbf{r}_1,t_1)$ and spin. 1^+ denotes $(\mathbf{r}_1,t_1+\Delta)$ with Δ a positive infinitesimal.

These equations may be iterated as desired, providing an infinite series with successively more accurate quantities defined as an expansion in lower-order terms. In practice, Γ is only evaluated in lowest order $[\Gamma(123)=\delta(12)\delta(23)]$ and the implicit series for Σ in

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Eqs. (2)–(4) is truncated at first order. This approach is the GW approximation,[3] in which Σ is expanded to first order in the dynamically screened Coulomb interaction and the dressed Green function,

$$\Sigma(1,2)=iG(1,2)W(1^{+},2) . \tag{6}$$

In order to obtain reasonable results in practice, both G and W are evaluated as accurately as possible in an *ab initio* numerical calculation. Much of the effect of exchange and correlation terms on the screening, which can be introduced with the iteration of Eqs. (2)–(4), is included here in the dielectric matrix by going beyond the RPA. In addition, the energy dependence of the Green function is obtained from the self-consistent quasiparticle spectrum, allowing for an improvement on the dressed Green function. Both of these features are needed to account properly for the bandwidth reduction.

Once the Green function and screened interaction are determined as discussed below the quasiparticle energy is calculated to first order by

$$E^{\mathrm{qp}}_{n\mathbf{k}}=\varepsilon^{\mathrm{LDA}}_{n\mathbf{k}}+\langle n\mathbf{k}\,|\,\Sigma(E^{\mathrm{qp}}_{n\mathbf{k}})-V^{\mathrm{LDA}}_{\mathrm{xc}}\,|\,n\mathbf{k}\rangle . \tag{7}$$

Also, in the present study, only the real part of the energy corrections is evaluated; lifetime effects are neglected.

In principle, the effect of vertex corrections on the self-energy [i.e., terms going beyond Eq. (6)] should be investigated. The importance of these corrections is uncertain, and numerical estimates of their significance from previous model calculations vary.[5,6] However, inclusion of the full vertex correction is not currently feasible, and lacking a reasonable approximation, we do not evaluate Γ beyond lowest order. In actual application, the GW approximation has been found to be quantitatively successful for a wide range of crystalline systems.[2,8]

B. Evaluation of the Green function

The Green function G is obtained in the quasiparticle approximation, where upon Fourier transforming the time argument,

$$G(\mathbf{r},\mathbf{r}',\omega)=\sum_{n,\mathbf{k}}\frac{\psi_{n\mathbf{k}}(\mathbf{r})\psi^{*}_{n\mathbf{k}}(\mathbf{r}')}{\omega-E_{n\mathbf{k}}-i\eta} . \tag{8}$$

ψ are the quasiparticle wave functions (which can be taken to be the LDA wave functions[8]), E is the quasiparticle energy spectrum, and η is a positive infinitesimal for quasiparticle energies $E_{n\mathbf{k}}$ below the Fermi energy and a negative infinitesimal for energies above.

The wave functions are evaluated in a LDA calculation using norm-conserving pseudopotentials.[14] A bcc structure is assumed in the calculation with an experimental lattice constant of 5.225 Å.[15] The Kohn-Sham method[16] is employed with exchange-correlation effects included using the Ceperley-Alder results for the homogeneous electron gas.[17] This treatment is similar to that of Northrup *et al.*[2] except a partial core correction[18] is used for treating the valence-core exchange-correlation in the present calculation to account for the larger core size of potassium.

The energy spectrum $E_{n,\mathbf{k}}$ is modified iteratively in calculating G and Σ. At each step, an approximately self-consistent input quasiparticle spectrum E is obtained by fitting the quasiparticle energies from the previous iteration to an overall additive shift and scaling from the LDA bands (i.e., $E=a+b\varepsilon^{\mathrm{LDA}}$). The iterations are stopped when the E spectrum differs from E^{qp} by typically 0.05 eV. This self-consistency was found to be necessary to obtain results in agreement with experimental values for sodium.[2] It has a significant effect on the occupied bandwidth results for potassium, as well. In principle, different parameters for the fit are needed for different bands. However, it was found that using only one pair of parameters for all bands yielded the same result for the lowest band (of interest here) as using one set of parameters for the lowest band and a second set for all others.

C. Evaluation of the screened Coulomb interaction

The dynamically screened Coulomb interaction can be defined in terms of the frequency-dependent time-ordered dielectric function and the bare Coulomb interaction as

$$W(1,2)=\int d(3)\epsilon^{-1}(2,3)v(1,3) . \tag{9}$$

The dielectric function may be written as a functional derivative:[3]

$$\epsilon^{-1}(2,3)=\frac{\delta V_{\mathrm{tot}}(2)}{\delta V_{\mathrm{ext}}(3)} \tag{10}$$

with $\delta V_{\mathrm{tot}}=\delta V_{\mathrm{ext}}+v\delta\rho$, and δV_{ext} is the external perturbation. In the static case, this may be obtained as a ground-state quantity in the density-functional formalism from the independent particle linear response polarizability χ_0:

$$\epsilon^{-1}=1+v(1-\chi_0 v-\chi_0 K_{\mathrm{xc}})^{-1}\chi_0 \tag{11}$$

where $K_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')=\delta V_{\mathrm{xc}}(\mathbf{r})/\delta\rho(\mathbf{r}')$ which is, however, a local function in the local-density approximation.

The dielectric screening is in general a function of both $\mathbf{r}$ and $\mathbf{r}'$ for a crystal due to the nonuniform charge density of the system, that is, the effect of local fields. In a momentum-space representation

$$\delta V_{\mathrm{tot}}(\mathbf{q},\omega)=\int d\mathbf{q}'\epsilon^{-1}(\mathbf{q},\mathbf{q}';\omega)\delta V_{\mathrm{ext}}(\mathbf{q}',\omega) . \tag{12}$$

The crystalline periodicity permits the expression of the screening as a matrix in reciprocal lattice vectors $\mathbf{G}$ and $\mathbf{G}'$:

$$\epsilon^{-1}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}';\omega)=\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q};\omega) . \tag{13}$$

The dielectric matrix was calculated with reciprocal lattice vectors $\mathbf{G}$ and $\mathbf{G}'$ of magnitude up to $5k_F$ where $k_F=0.395$ a.u. is the free-electron Fermi wave vector for potassium. Local fields were found to have little or no effect in the results for lithium and sodium. There is similarly no effect in potassium to within the accuracy of this method. In fact, a similar calculation yields the same bandwidth when applied to the electron gas with the average electron density of potassium.[19,20] In the calculation, the static, independent-particle polarizability is calculated by an Adler-Wiser-type perturbation method from the LDA wave functions and energy spectrum.[9] Forty bands are included in the perturbation expansion. The static dielectric matrix is then calculated using Eq. (11). Finally, the frequency-dependent dielectric matrix, $\epsilon^{-1}_{G,G'}(\mathbf{q},\omega)$, is obtained in a generalized plasmon-pole approximation,[8] in which energy-dependent screening is obtained from the static screening by fitting the response to the Kramers-Kronig relations and the f-sum rules.[8]

Two dielectric functions are evaluated: the first is in the random-phase approximation with K_{xc} set to zero, while the second (LDA) includes the electron-electron exchange and correlation effects on the response function using the LDA K_{xc}. We stress that both dielectric functions employ the LDA wave functions and energies in evaluating matrix elements, but the LDA dielectric function includes the effects of exchange and correlation in calculating the response. The RPA dielectric function, of course, only includes the Coulomb interaction.

III. QUASIPARTICLE RESULTS

The LDA value of the occupied valence bandwidth of potassium is 2.27 eV. This is reduced in the GW approximation with the LDA dielectric function and the self-consistent energy spectrum in the Green function to a bandwidth of 1.58±0.1 eV. This compares well with a recent photoemission experiment which yielded a result of 1.4 eV.[7]

There are two significant contributions to the bandwidth reduction which make our results differ from the electron-gas results of Ref. 3. First, the energy self-consistency in the evaluation of G in Eq. (8) was found to be significant in the cases of lithium and sodium, causing additional decreases in the occupied bandwidth and bringing it into agreement with experiment. The self-consistency for potassium has the same effect; a non-self-consistent calculation with the LDA eigenvalues in Eq. (8) yields a smaller reduction of the bandwidth to 1.8 eV. Second, use of the RPA dielectric function results in a larger bandwidth than is observed experimentally. When the RPA screening is used in W with a self-consistent energy spectrum in G the bandwidth is also only reduced to 1.8 eV. Thus the RPA reduction is 0.47 eV versus the full reduction of 0.69 eV. Both effects must be included to obtain a result in agreement with sodium photoemission experiments. Our calculated bandwidth is still some 0.1 eV larger than the photoemission result,[7] which may be due to the neglect of vertex corrections. Such terms may reduce the bandwidth further, although their quantitative importance remains an open question.[5,6]

The self-energy correction $E^{\text{qp}}-\varepsilon^{\text{LDA}}$ using the LDA and the RPA dielectric functions is plotted versus wave vector in Fig. 1. Coincidentally, equal values of the bandwidth reduction are obtained in using the RPA dielectric function together with a self-consistent energy spectrum in the Green function for Σ as in using dielectric screening beyond RPA, but without energy self-consistency. However, this was not the case for sodium; the self-consistent RPA bandwidth reduction was less than the not-self-consistent, beyond-RPA result.[2]

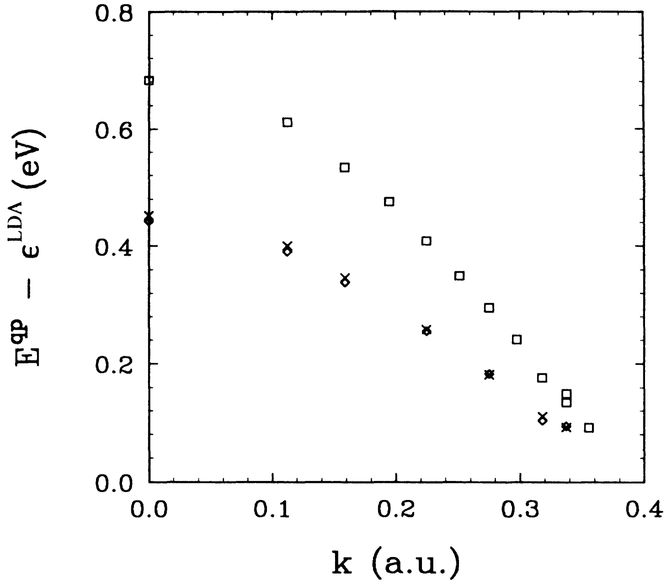

FIG. 1. Self-energy correction from the LDA band eigenvalues for some of the occupied states. Three results are plotted: RPA dielectric screening of W with self-consistent quasiparticle energies in G (×); LDA dielectric screening (see text) with self-consistent quasiparticle energies in the Green function (□); non-self-consistent calculation with the LDA dielectric screening (◇).

The effect of going beyond the RPA dielectric screening can be understood[2] in terms of a Coulomb hole-screened exchange picture for the self-energy.[3] The screened exchange contribution to Σ is simply the usual Hartree-Fock exchange term, but with an energy-dependent screened Coulomb interaction instead of the bare interaction. The Coulomb hole term represents the

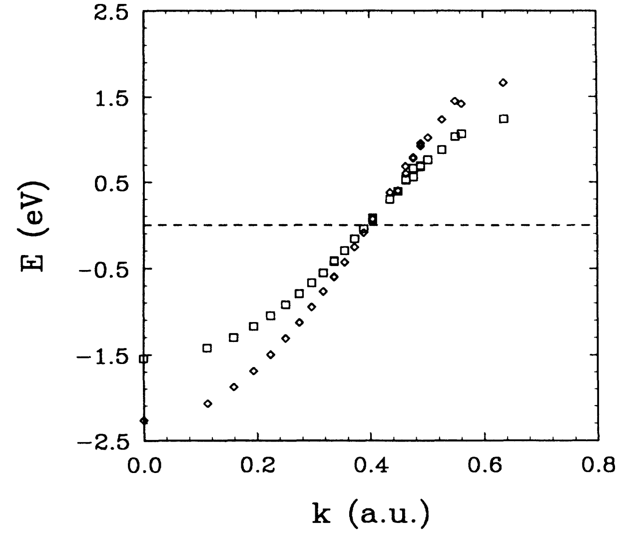

FIG. 2. Potassium quasiparticle energies (□) and LDA band eigenvalues (◇) of the first band for the 29 special points evaluated. The Fermi energy is set at zero.

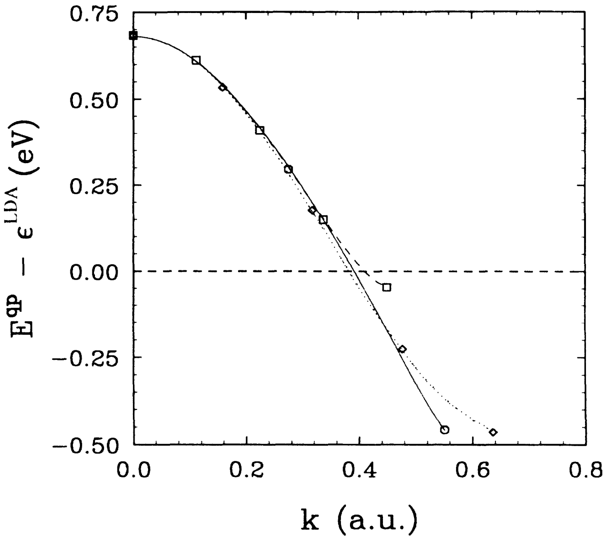

FIG. 3. Directional dependent of the self-energy correction. The calculated points and a fit for $E^{qp}-\varepsilon^{LDA}$ are plotted along three symmetry directions; · · · · and ◇ are in the (100) direction; — — — and □ in the (110); and —— and ○ in the (111).

additional contribution to Σ from the correlation of an electron polarizing the surrounding electron gas. In the plasmon-pole model this is simply the second-order interaction of a quasiparticle with the plasmon modes. The bandwidth reduction (equivalently, the effective-mass enhancement) thus resembles the polaron problem. The total enhancement depends on the appropriate energy denominator for the perturbation averaged over plasmon modes. The LDA dielectric function [i.e., the dielectric with K_{xc} included in Eq. (11)] enhances screening over the RPA, since the inclusion of exchange-correlation reduces the energy cost of an inhomogeneous charge density in the electron-gas response. The enhanced screening reduces the dispersion of the plasmon, and so the energy denominator in determining the Coulomb hole is reduced. Thus, the added bandwidth reduction derives from the increased coupling to the plasmons.

The result for the quasiparticle band structure closely resembles the LDA band, but with a scaled-down bandwidth (Fig. 2). There is also a very weak directional dependence of the quasiparticle band structure which differs from the original LDA band; the difference is plotted in detail in Fig. 3. A fit is made to the quantity $E_{n\mathbf{k}}^{qp}-\varepsilon_{n\mathbf{k}}^{LDA}$ defined at 29 special points in the irreducible Brillouin zone by using an eighth-order polynomial with the appropriate cubic-symmetry relations between the coefficients. Sixth- and tenth-order fits were also tried, with the tenth-order fit showing signs of numerical instability. All three fits reproduced the features of Fig. 3, but the detailed shape of the fitted Fermi surface changes significantly for the different order polynomial fits. This is not unexpected, since the limited number of points evaluated leaves the fit unreliable on the fine scale needed for the Fermi surface. The Fermi surface deviates from a sphere by only a few parts in 10^3.[21]

IV. SUMMARY AND CONCLUSIONS

As in a previous study of lithium and sodium,[2] we show that the inclusion of exchange-correlation effects in the screened Coulomb interaction and of energy self-consistency in the Green function is necessary to obtain an accurate self-energy in the *GW* approximation. Part of the bandwidth reduction from the LDA calculation is obtained using the RPA dielectric function together with a self-consistent energy spectrum in the Green function. The remaining reduction is obtained from the inclusion of LDA exchange-correlation effects (going beyond the RPA) in the dielectric screening. The effect of vertex corrections, however, has not been examined. Finally, we find that the quasiparticle calculation also changes the directional dependence of the eigenvalues from the LDA band structure by a very small amount.

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[1] E. Jensen and E. W. Plummer, Phys. Rev. Lett. **55**, 1918 (1985).

[2] J. E. Northrup, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **59**, 819 (1987).

[3] L. Hedin, Phys. Rev. **139**, A796 (1965); L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 25.

[4] M. Schreiber and H. Bross, J. Phys. F **13**, 1895 (1983).

[5] X. Zhu and A. W. Overhauser, Phys. Rev. B **33**, 925 (1986).

[6] T. K. Ng and K. S. Singwi, Phys. Rev. B **34**, 7743 (1986).

[7] E. W. Plummer, Phys. Scr. T **17**, 186 (1987).

[8] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); Phys. Rev. B **34**, 5390 (1986).

[9] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5585 (1987); **35**, 5602 (1987).

[10] R. H. Kingston, Phys. Rev. **84**, 994 (1951).

[11] R. S. Crisp, Philos. Mag. **5**, 1161 (1960).

[12] P. R. Norris, Phys. Lett. **45A**, 387 (1973).

[13] P. N. First, R. L. Fink, and C. P. Flynn, J. Phys. F **17**, L29 (1987).

[14] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[15] C. S. Barrett, Acta Crystallogr. **9**, 671 (1956).

[16] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[17] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1783 (1982).

[19] I. W. Lyo and E. W. Plummer (unpublished).

[20] J. E. Northrup, M. S. Hybertsen, and S. G. Louie (unpublished).

[21] M. J. G. Lee and L. M. Falicov, Proc. R. Soc. London, Ser. A **304**, 335 (1968).