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Self-energy corrections in photoemission of Na

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We have calculated the photoemission spectra of Na, where self-energy corrections and surface effects are fully incorporated. The self-energy is calculated with the Rayleigh-Schrödinger perturbation method. The energy shifts in both the initial states and the final states are specifically demonstrated by comparing the calculation with the measured results of Plummer and coworkers. It is found that both the imaginary part and the real part of the self-energy contribute to the observed large bandwidth reduction in Na. We believe these effects to be important, in general, in analyzing photoemission spectra.

The band structure of Na is generally believed to be well represented by nearly-free-electron (NFE) bands. However, Jensen and Plummer[1] (JP) found that their photoemission spectra from the Na(110) surface could not be readily explained with the NFE band. Two outstanding discrepancies are the following: (1) the observed bandwidth is 2.5 eV instead of 3.2 eV, the NFE bandwidth, and (2) there exist sharp peaks in a "gap" at photon energies $\hbar\omega \sim 35$ eV where no structure was predicted (see Ref. 1). These findings cast serious doubts[1,2] on our basic understanding of a system as simple as Na. The large bandwidth narrowing was viewed as evidence of inaccuracies in the many-body theory,[1] and the peaks in the gap are taken as indications that the conduction band is severely distorted.[1,2]

Shung and Mahan pointed out (Ref. 3, referred to as I) that the short mean free path (MFP) of photoelectrons is important since, as a result of it, photoexcitations are not strictly vertical. A short MFP also means that only electrons from the surface region can escape the metal and, hence, surface effects are important. It was shown in I that, when the finite MFP and surface effects are included, the presence of sharp peaks in the gap can be explained in accordance with the NFE band.

In this work we extend our calculation to include the self-energy of electrons $[\Sigma(k) = \Sigma_1(k) + i\Sigma_2(k)]$. We evaluate $\Sigma(k)$ using the Rayleigh-Schrödinger (RS) method and obtain results that are slightly modified from Hedin's.[4] The calculated spectra, after $\Sigma(k)$ is included, give a conduction band that agrees closely with the measured one—suggesting that the photoexcitations are between the quasiparticle states:

$$\epsilon(k) = \epsilon_0(k) + \Sigma(k); \quad \epsilon_0(k) = \hbar^2 k^2 / 2m \ . \qquad (1)$$

The importance of the self-energy shifts (i.e., Σ_1) has been stressed by many authors for various materials.[5,6] We emphasize that both Σ_1 and Σ_2 of the initial states and of the final states are included in this work, and all are found to be important. To our best understanding, this is the first such calculation where the surface effects are also incorporated.

The self-energies are calculated by the RS perturbation theory and are done within the random-phase approximation (RPA). In this theory the quasiparticle energy of an unoccupied state at momentum k is obtained as the total energy change of the interacting electron system when an electron is added to that state. For an occupied state k, its

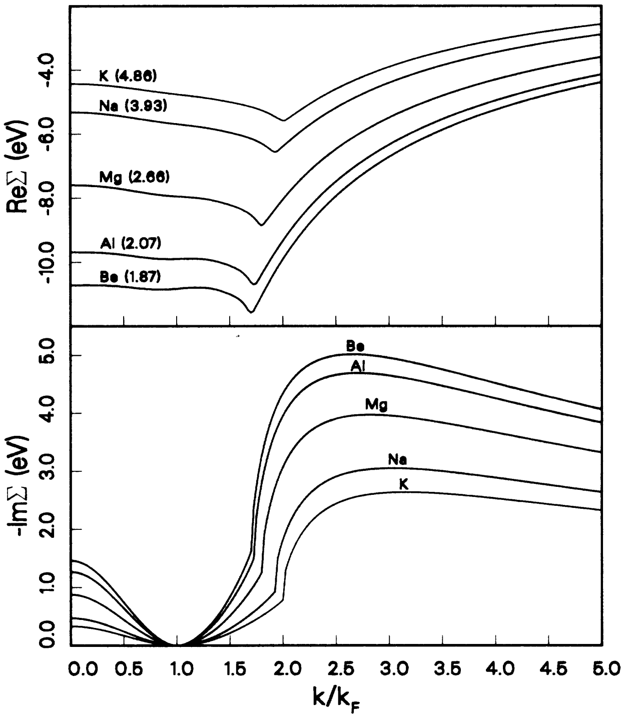

FIG. 1. Self-energy shifts, as a function of wave number, which were obtained for some simple metals. The r_s values which were used are shown in parentheses. We should point out that, for $k < k_F$, the sign of the imaginary part of the self-energy given here is that for a hole, and not for an electron.

quasiparticle energy is the negative of the energy change when the electron is removed. The energy so obtained is an explicit function of momentum and not energy, as is expressed in Eq. (1). Details of the RS method can be found in Ref. 7. Figure 1 shows our results for some common simple metals, with both the real and the imaginary parts given.

We find that the bandwidth of Na is 2.87 eV, which differs slightly from other calculations [2.97 eV (Ref. 4) and 2.5–2.6 eV (Ref. 5)] where the so-called *GW* method was employed. In that approach, the real part of the self-energy is obtained by solving Dyson's equation for the Green's function. The proper self-energy insertion is calculated to first order of the screened interaction, and depends explicitly on both momentum and frequency. To get reasonable results one has to replace the internal undressed Green's functions with the dressed ones, and this is done in an approximate way by replacing the unperturbed energies in the Green's functions by the shifted ones. By making this replacement, one effectively sums an infinite class of self-energy diagrams. It has been argued[7] that in this procedure important diagrams are multiply counted and that it is difficult to know how good the results thereby obtained are. One can get some clues from the similarities to the polaron problem (see, e.g., Ref. 8). The self-energy diagram looks very much the same in that problem. The only difference is that the screening there comes from the lattice and not from the electrons themselves. In the polaron problem, the RS method works much better than the *GW* method except in the region where the polaron starts decaying via the emission of phonons. Here, that region corresponds to the region around the plasmon energy above the chemical potential, where the electron starts to lose energy via the emission of plasmons.

In the present work, as our interest is not specifically on the plasmon structure, the RS method seems a reasonable one to choose. Besides, it is easy to apply, and is economic with respect to computing time. We note that Hybertsen *et al.*[5] calculated numerically the self-energy of Na using the GW method, where the self-consistency in energy is retained. They find a large reduction in the bandwidth of Na (0.7 eV) due to Σ_1 alone, while we find that Σ_2 is also important (see below).

As in I, we employ Mahan's theory of photoemission[9] in our calculation. With the self-energy included, the normal-emission spectrum is expressed by (the initial momentum $k_i = k_{i\parallel}$)

$$\frac{d^2 I}{dE\,d\Omega} = \frac{em}{2\pi^2}\int d\epsilon\,\hbar p \langle \phi^{>}(p) \,|\, H' A(\epsilon) H' \,|\, \phi^{>}(p)\rangle \delta(E - \epsilon - \hbar\omega + V_0) \;, \tag{2}$$

where $E = \hbar^2 p^2/2m$ is the photoelectron energy measured externally, V_0 the surface barrier, and $H' \sim \mathbf{A}\cdot\mathbf{p}$ the interaction that induces the excitation. $\phi^{>}(p)$ is the scattered wave in the final state and $A(\epsilon)$ the spectral function for finding an electron at ϵ. When the Coulomb interaction is neglected we can put $A(\epsilon) = \sum_{k_i} |k_i\rangle\langle k_i|\,\delta(\epsilon - \epsilon_0(k_i))$ and Eq. (2) reduces to Eq. (1) of I. The effect of the Coulomb interaction is incorporated by replacing $\epsilon_0(k_i)$ by $\epsilon(k_i) - \Sigma(k_F)$ in $A(\epsilon)$. The subtraction of $\Sigma(k_F)$ is to avoid double counting the self-energy shift, since $\Sigma(k_F)$ is already included in V_0 (see below). Also, because $\Sigma_2(k_i) \neq 0$ (except at k_F), the δ-function in $A(\epsilon)$ becomes a Lorentzian of width $\Sigma_2(k_i)$. Thus far, we have explicitly included the self-energy of the initial states in our theory. For the final states, the self-energy part will appear implicitly in $\phi^{>}$, and will be discussed later.

Almbladh,[10] in a rigorous derivation using many-body techniques, obtained an expression similar to Eq. (2). He further showed that, with proper approximations, the many-body interaction H', can be transformed into the form $(i\omega)^{-1}[\mathbf{A}_z \partial V(z)/\partial z]$, where $V(z)$ is an effective one-body potential. In his derivation, Almbladh answered one often-debated question on whether a decaying part in $\phi^{>}$ would lead to a violation of selection rules in photoemission.[11,12] Almbladh showed that it would not. In the following we separate $V(z)$ into a surface part $V_s(z)$ and a bulk part $\sum_G V_G \exp(-iGz)$, as was done in I.

We use Lang and Kohn's[13] surface potential for $V_s(z)$ and then find $\phi^{>}$ and ϕ accordingly. ϕ's are already determined in the Lang-Kohn self-consistent calculation, but $\phi^{>}$'s are not and require further considerations. Quasiparticle states are calculated with an effective Hamiltonian $H = T + V_H(z) + \Sigma(k,z)$, where T is the kinetic energy, V_H the Hartree potential, and $\Sigma(k,z)$ the k-dependent self energy , or the exchange-correlation energy. In the vacuum ($z < 0$) $\Sigma(k,z) = 0$, hence, electrons experience a surface barrier of height $V_0(k) = V_H(-\infty) - [V_H(\infty) + \Sigma_1(k,\infty)]$. Clearly this barrier is k dependent. The constant barrier V_0 in Eq. (2) corresponds to $V_0(k_F)$. It is easily seen that, for an electron at k_j, the barrier is scaled from V_0 by a factor of $R(k_j) = \{V_0 - [\Sigma_1(k_j) - \Sigma_1(k_F)]\}/V_0$. We can thus use the effective Hamiltonian $H = T + R(k_j)V_0(z)$ and suitable boundary conditions of incoming waves[11] to evaluate $\phi^{>}$, where $V_0(z)$ is the unscaled Lang-Kohn potential. The correctness of the energy relation can be checked as follows. An excited electron at energy $\epsilon(k_j) = \epsilon(k_i) + \hbar\omega$ in the bulk must appear externally at the energy $E = \hbar^2 p^2/2m = \epsilon(k_j) - [V_0 + \Sigma(k_F)]$. Since $\phi^{>}(p)$ oscillates $\sim\exp(ipz)$ [$\sim\exp(ik_j z)$] outside (inside) the bulk, the barrier height is $\hbar^2(k^2 - p^2)/2m$, which equals $R(k_j)V_0$ as expected. Finally, a decaying part $\exp[-z/2\lambda(k_j)]$ is added to $\phi^{>}$ if $z > 0$, where $\lambda(k_j)$ is the MFP equal to $\hbar^2 k_j/2m\Sigma_2(k_j)$. As we noted earlier, this procedure is reasonable and does not cause selection-rule violations.

The effects of broadening (i.e., $\Sigma_2 \neq 0$) in initial states[3] and final states[14] were discussed previously. The main effect from the inclusion of Σ_1 in the present work is to shift the peak positions in the spectra, and to reduce the bandwidth. The shape of spectra (e.g., the Fermi-edge structures) remains essentially unchanged. In the following, we will focus on the energy shifts due to the initial and final states, respectively. The parameters used in this calculation are the same as before,[3,14] but instrumental broadening is now 0.05 eV in width (it was 0.3 eV in I) in order to cope with the improved experimental resolution.[15]

The self-energy shift in final states can be most easily seen from the peaks in the forbidden gap, since these peaks have the same initial states at $\epsilon(k_F)$ and thus, energy shifts only involve the final states. In I it was predicted that these peaks would be weak and narrow inside the gap. Such effects were recently observed,[15] but discrepancies were also found concerning the gap location.[14] Figures 2 and 3, respectively, show the width of the peaks and the edge intensity [at $\epsilon(k_F)$] around the gap region. The measurements at $\hbar\omega \sim 30$ eV are marred by *LVV* Auger emission and by emission from the $2p$ core states.[14] Nevertheless, the measured results (crosses) demonstrate, unmistakably, the very distinctive structures (dips) at the gap region.

The calculated results, whether with (circles) or without (triangles) $\Sigma_1(k)$, show the similar structures around the gap. However, much better agreement is obtained only if the self-energy is included. This is clear evidence regarding the energy shifts of the final states: The gap is shifted to higher energies and becomes slightly wider (see the figures). The calculation also reveals the experimental finding[15] that, with the improvement on instrumental resolutions, the width of the peaks inside the gap is reduced to as little as 0.35 eV (Fig. 2) (peak width was 0.8 eV with poorer resolutions[1,3]). Such good agreements are strong indications of the validity of our photoemission theory; they also suggest the correctness of our self-energy calculation. We remark that, when there is no distinctive peak at $\sim\epsilon(k_F)$ (e.g., far from the gap), the Fermi-level intensity (and the width also) cannot be determined with certainty. This inaccuracy is relevant to, but seems too small to account for, the differences in intensity at energies away from the gap (Fig. 3). A better calculation for the lattice potentials V_{110} and V_{220} is probably necessary to resolve this problem.

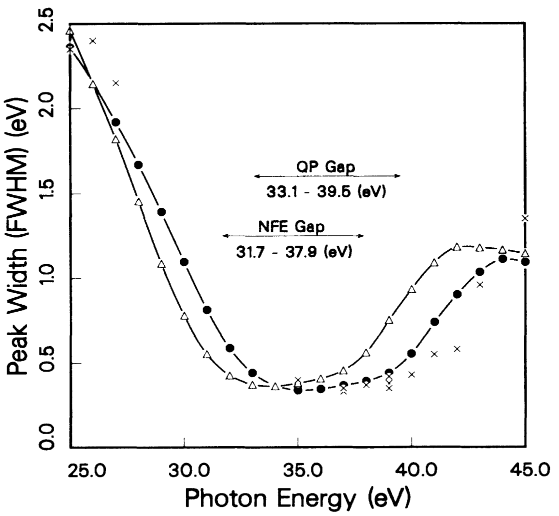

FIG. 2. This figure represents the peak width at $\hbar\omega$ around the forbidden gap. The crosses indicate the measured results (Ref. 17). The connected circles (triangles) are calculated with (without) the energy shifts due to Σ_1. The quasiparticle gap is denoted QP.

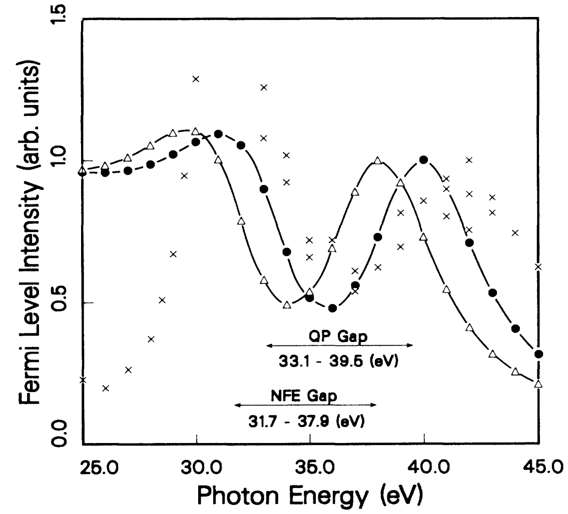

FIG. 3. The peak intensity [at $\sim\epsilon(k_F)$] is given as a function of $\hbar\omega$. Notation is the same as in Fig. 2.

Peak positions, in terms of their initial states, are given in Fig. 4. The quasiparticle bands (with Σ_1 included) are represented by the solid curves, which are narrower than

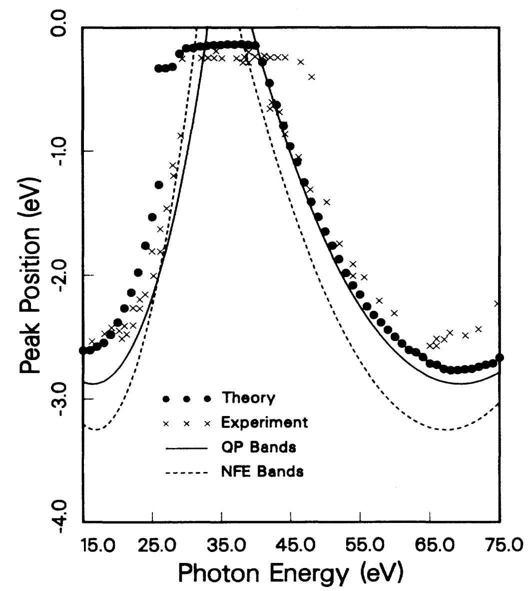

FIG. 4. Peak positions are shown as a function of $\hbar\omega$. Experimental data are from Ref. 1. A smaller instrumental broadening effect is used in the calculation (see text), which causes the peaks inside the gap to move closer to the Fermi level (see I).

the NFE bands (dashed curves) by 0.37 eV. In photoemission, the broadening of states and the surface effects both contribute to the bandwidth reduction.[3,14] The main broadening effect is to shift the bottom of the band upwards, since these transitions correspond to broader initial states (Fig. 1). This is most easily seen at 40 eV $< \hbar\omega < 70$ eV, where the surface effects are small.[14] When $\hbar\omega < 30$ eV, surface effects become strong enough to shift the peaks to higher energies as well. Both the calculated and measured results[1] demonstrate such shifts (from the quasiparticle band) although the shift, due to the surface effects, seems too large in the calculation. Our results show that the bandwidth of Na is 2.6–2.78 eV, and the measured width is 2.5 ± 0.1 eV. In the calculation, we did not include a band-bending effect due to the lattice potential. Mahan[9] estimated that this effect accounts for 0.06 eV reduction in the bandwidth of Na. If we take this band bending into consideration, we find no more than 0.1 eV in discrepancy with JP's measured bandwidth. It is important to notice that the broadening of electronic states, as well as the surface effects, affects the accuracy of a determination of band structures via photoemission measurements. Such effects, therefore, should be included when comparing theoretical band structures with experiments. Unfortunately, they have mostly been neglected.[5,6] More discussion concerning the effects due to Σ_2 are given in Ref. 14.

In summary, we have calculated the self-energy of electrons in Na, and included it in our theory of photoemission. It is found that both the real and the imaginary parts of the self-energy are keys to the understanding of JP's photoemission spectra.[1,15] Good agreement with the experiment suggests that the conduction band of Na can be described by a NFE band, which is modified with the self-energy correction due to many-body interactions. We note that Overhauser[2] provided an alternative explanation of JP's results, in which the conduction band of Na is severely distorted due to charge-density waves (CDW's). Our comments on CDW's in Na are given in Refs. 12 and 14. Lastly, we conclude that the self-energy effects, in addition to the surface effects (see I), should always be taken into account when analyzing photoemission spectra of Na, and of other materials too.

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