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Effect of ground-state and excitation potentials on energy levels of Ni metal

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Self-consistent energy-band calculations for paramagnetic Ni have been performed in an effort to compare ground-state and excitationpotential prescriptions; potentials of the Hartree-Fock-Wigner-Seitz and Hedin-Lundqvist type are examined. We find the bandwidth and placement of the Fermi level within the bands to be rather insensitive to the choice of potential, while the absolute position of the bands with respect to the appropriate reference energy is potential dependent. Use of the Hedin-Lundqvist excitation potential instead of the ground-state potential produces level differences no greater than 0.1 eV.

I. INTRODUCTION

The theory of solids is plagued by the fact that electron-electron interactions involve a nonlocal electron potential. In a classic series of papers Hohenberg, Kohn, and Sham[1] discussed the circumstances under which a local potential, i.e., one that depends only on the coordinates of the sampling electron, could replace the exact nonlocal form. They observed that a local potential could yield ground-state properties such as the charge density and Fermi surface and that a *different* local potential could describe the excitation spectrum of states away from the Fermi surface.[2]

In general the crystal potential is dominated by the Hartree contribution. The exchange-correlation part of the potential is often written

$$V_{xc}(r) = -A[\rho(r)]^{1/3} \quad , \tag{1}$$

where $\rho(r)$ is the local electron number density. On physical grounds Slater and co-workers have employed several, nearly equal, values of the prefactor A in constructing ground-state potentials. Hedin and Lundqvist,[3] exploiting the dielectric-function results of Singwi *et al.*,[4] have derived a ground-state potential for which A is a slowly varying function of ρ. This potential yields results quite similar to those of the Slater prescription. Hedin and Lundqvist have also defined an excitation potential which depends on a state's one-electron energy measured with respect to the Fermi energy ϵ_F. In this paper we calculate self-consistent energy bands for paramagnetic fcc nickel employing the two Hedin-Lundqvist potentials; comparison is also made with previous results based upon the Hartree-Fock-Wigner-Seitz approximation. In addition to factors such as d-band width and the relative position of the d and non-d conduction bands we investigate the absolute position of the bands; absolute placement of the bands is crucial to an understanding of work functions. The predictions of the excitation potential for the minima of the d and conduction bands will be compared with the predictions of the ground-state potentials. To our knowledge this is the first such comparison[5] for a transition metal.

Briefly our results are as follows: (i) As is the case for most band calculations for fcc nickel we find that the bandwidth and the placement of the Fermi level within the bands are rather insensitive to the potential choice. (ii) On the other hand, the absolute placement of the bands relative to the crystal zero is sensitive to the choice of potential; for the case of the Hedin-Lundqvist potential the bands lie too shallow in energy. (iii) Finally, we find that differences in energy levels arising from use of either the Hedin-Lundqvist ground state or excitation potential are small, no more than 0.1 eV, which is at the limit of present experimental resolution.

II. CALCULATION

The calculation combines augmented plane wave and interpolation scheme methods in a two-step procedure. First, for a given potential the wave functions are calculated at selected energies. These results together with an interpolation scheme[6] permit the calculation of a density of states and, more importantly, a density $\rho(r)$. Second, a new potential can be constructed from the density, band energies determined at a few high-symmetry points, and the parameters of the interpolation

TABLE I. Results for energy levels (in eV) at certain selected points in the zone as given by three calculations. The d-band width is slightly larger than the difference between X_5 and X_3. The first column is from a renormalized-atom-scheme calculation using a potential (HFWS) with the hole localized in the center of the cell. A self-consistent version of that calculation is listed in the next column. The final column gives the result of using a potential which includes the fact that the hole really follows the electron.

"Place" in band	HFWS[8]	Self-consistent HFWS[10]	HL
Γ_1	−10.5	−12.9	−9.5
X_3	− 7.0	− 9.1	−4.2
X_5	− 2.5	− 5.2	−0.3
ϵ_F	− 2.7	− 5.4	−0.5

scheme rescaled by these new band energies. This procedure is iterated to self-consistency—i.e., until energies change by less than 0.005 Ry. A special aspect of the calculation is that the electron density is normalized to the Wigner-Seitz cell. Accordingly the zero of energy is the crystal zero, V_0, i.e., the vacuum zero shifted by the metal's surface dipole energy D. This fact allows us to discuss the absolute placement of the *ground-state* levels. In order to calculate the excited-state levels we use the appropriate excitation potential. A discussion of both potentials and their use in a calculation is given in the Appendixes.

III. RESULTS

In Table I the results for energies at a few selected points in the Brillouin zone are given. The Appendixes outline the procedures by which these energies are calculated. For the ensuing discussion we note that ϵ_{Γ_1} is the bottom of the non-d-band. The width of the d band is here taken to be[7] the difference between ϵ_{X_5} and ϵ_{X_3}.

The first column of figures lists the results of Hodges, Watson, and Ehrenreich.[8] In this work a Hartree-Fock (HF) potential, with either a d or s hole (as appropriate) centered at the nucleus, is used in the renormalized atom method.[9] This approximation (denoted HFWS, the WS standing for Wigner-Seitz who first proposed this self-Coulomb hole approximation) gives a fairly broad d band with a width of 4.5 eV and a Fermi level lying 0.2 eV below the top of the d band in a high density-of-states region. This latter feature is common to the other two results we discuss.

The effects of doing a self-consistent calculation are shown in the second column.[10] The basic procedure is similar to that described in Sec. II. Since in the self-consistent result the charge spreads out slightly in the cell, the effective attractive potential is stronger, all the levels drop, and the d band narrows to about 3.9 eV. The generally accepted experimental value for the d-band width is[11] $3-3\frac{1}{2}$ eV; in contrast with the results for neighboring metals such as Fe, Co, and Cu, band theory consistently overestimates the Ni bandwidth.

Finally in the last column of Table I are the results of our self-consistent calculation using the ground-state potential of Hedin-Lundqvist[3] (labeled HL in the table). We observe that, while the d-band width is the same as for self-consistent HFWS, both the d and s bands have moved upward relative to the crystal zero. The qualitative reason for this is that the HL potential incorporates an exchange-correlation hole which is more diffuse than in the WS approximation, for which the hole is centered in and confined to the WS cell. Accordingly, in the HL approximation the electron sees a weaker effective potential and the levels rise relative to HFWS results.

At this juncture we may compare our results with those of other calculations. We note that for the HL potential the factor A of Eq. (1) hovers near a value corresponding to $\alpha \sim 0.7$, while the HFWS approximation may be taken to loosely correspond to $\alpha \sim 0.9$. Connolly[12] and Callaway and Wang[13] have performed self-consistent band calculations for ferromagnetic Ni with $\alpha = \frac{2}{3}$. Their results for the d-band width and $\Gamma_1 - X_3$ level separations agree well with each other; they obtain a d width of 4.0 eV and $\Gamma_1 - X_3$ differences of 4.7 and 5.4 eV for the majority and minority spins, respectively. These values compare reasonably with our results (see Table I) except that we find smaller $\Gamma_1 - X_3$ separations for the HFWS calculations; the smaller values are a direct consequence of the fact that HFWS may be crudely related to a density-dependent exchange-correlation potential having α nearer to unity. Without detailed information on the treatment of the energy zero in the other calculations we cannot compare absolute band positions.

One feature of the upward shift of the levels in the HL approximation is that the Fermi level is placed 0.5 eV below the crystal zero V_0. The work function for Ni is 5.0 eV, and this equals the surface dipole energy D plus $(V_0 - \epsilon_F)$. Dipole-term estimates suggest[14] that D is of the order of 1–2 eV. Admittedly, this estimate is based on results for simple, polyvalent, and noble metals, but *not* for transition metals. In any event, unless the dipole term is grossly underestimated, the HL potential has placed ϵ_F substantially too high. It would appear that the exchange-correlation hole associated with the Hedin-Lundqvist, and for that matter the Slater, potential is too weak, placing the bands too shallow with respect to the crystal zero. (On the other hand, the WS approximation has placed them too deep.) In one instance of this, Janak *et al.*, in their study[15] of Cu, found that to reproduce the experimental Fermi surface it was necessary to invoke a more localized hole, i.e., a larger value of A in Eq. (1) than that supplied by either the HL or Slater potentials.

Despite the fact that both the HL and Slater potentials place the bands too shallow, this does not necessarily imply that cohesive energies (E_c) calculated with these potentials will be unreliable. Calculations for sodium[16] and lithium[17] with $\alpha = \frac{2}{3}$ have yielded E_c results in excellent agreement with experiment. The principal reason for this is that the two-electron terms have to be properly included in the total energy computations, which diminishes the importance of absolute one-electron-level position. The absolute position of the bands is consequently an even more stringent test of a band-structure potential than the value of E_c to which it leads. We have not calculated E_c for the HL potential; results for the 3d and 4d transition metals in the HFWS approximation, both non-self-consistent[18] and self-consistent,[10] are in good overall agreement with one another and with experiment.

Another aspect connected with the upward shift of the bands concerns the relative placement of the d and non-d-bands and the number of holes in the d band. An argument that the d band should be shifted down relative to the non-d band by 0.4 eV is as follows. Ferromagnetic Ni has a moment of 0.59 μ_B.[19] Scott and Reck[19] have divided the magnetization of Ni into orbital and spin components, obtaining a spin moment of $0.55\mu_B$. On simple, intuitive, and single-particle grounds the *paramagnetic* hole count (for both spins) equals, or is slightly less than, the spin moment of ferromagnetic Ni. To produce a hole count for a single spin of $\frac{1}{2}(0.55)$, as compared with our calculated hole count of $\frac{1}{2}(0.59)$ per spin for the HL ground-state potential, the non-d-band must be raised ~0.4 eV relative to the d band. In summary, the ground-state HL potential works fairly well, but places both bands too high relative to the crystal zero with the d band lying a little too high relative to the non-d-band.

Finally we turn to the effect of using the HL excitation potential, which is slightly more attractive[20] than the ground-state potential for band states below ϵ_F. In contrast to the results for the ground-state potential, ϵ_{Γ_1} is lowered by 0.05 eV and the bottom of the d band by 0.08 eV. These shifts are small, but they are beginning to be accessible experimentally as evidenced by the recent investigations of Grobman and Eastman[21] for Ge. They report deviations of the order of 0.1 eV between experiment and what were, in effect, ground-state predictions for levels well away (~10 eV) from ϵ_F. Clearly both experimental resolution and theoretical calculations must be improved before such effects, arising from differences between the ground-state and excitation potentials, can be ascertained.

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APPENDIX A: DETAILS OF THE CALCULATION

The Schrödinger equation with a given band potential is integrated, and the energy at which a 4s-like orbital is flat at the Wigner-Seitz radius r_{WS} is determined; this energy corresponds to the Γ_1 level in the band structure. The energies at which a 3d orbital is flat and noded at r_{WS} are also found; these energies correspond closely[8] to the levels at X_3 and X_5 and thus may be used to specify the position and width of the d bands. Although the states determined by these Wigner-Seitz-type criteria are not precisely characterized by the wave vectors at the points X_3 and X_5 in the Brillouin zone, the (small) deviation from the energies at those points has been investigated.[22] This information on band extrema is fed into the Hodges interpolation scheme.[6] From iteration to iteration the scheme's d-d matrix elements are scaled by the d-band width, and the s- and d-band extrema determine the relative s- and d-band positions. The s-d hybridization and the plane wave pseudopotential matrix elements are not modified in a normal iteration. When convergence is almost achieved, the band potential at that stage is used in an augmented plane wave band calculation which, in turn, is fitted to determine all the parameters employed in the interpolation scheme, except for a spin-orbit constant.

A uniform mesh of 1877 points in $\frac{1}{48}$th of the Brillouin zone is used in the interpolation scheme to obtain the density of states and to determine ϵ_F. The d components of the interpolated eigenfunctions are found and a density of d states constructed. This, together with d functions obtained in the band potential at a set of energies, is used to make an accurate estimate of d-component contributions to the electron density. Non-d contributions to the electron density are obtained more crudely; namely, the charge density of an s-like orbital, determined at the energy $\epsilon = \epsilon_{\Gamma_1} + \frac{3}{5}(\epsilon_F - \epsilon_{\Gamma_1})$, is weighted by the non-d count. These band contributions to the density are added to that of a d^9s atom core which is held fixed during the course of these calculations. Using the full electron density, the band potential is reconstructed and the process repeated.

We emphasize that the interpolation scheme provides a detailed density of states that we use to find sampling energies at which to integrate for *d* wave functions. The *d* functions are obtained over the full Wigner-Seitz sphere; together with the *d* eigenvector weights, they allow the *d* charge density to be constructed with considerable accuracy. Our principal assumption is that the interpolation scheme yields an accurate estimate of the *d* weights; in doing this, we obtain a $\vec{k}$-space sampling much more detailed than that of most self-consistent band calculations (see, for example, Refs. 12 and 13). Our primary source of error is the crude sampling of the non-*d* components of the charge density. We estimate that our use of a single, average *s*-like wave function may lead to an uncertainty as great as a few tenths of an electron volt in the absolute position of the bands, but the error in relative band placement is much smaller.

APPENDIX B: CONSTRUCTION OF POTENTIALS

Ground-state potential

One point to keep in mind is that the local density $\rho(r)$ defines a *local* interelectronic spacing $r_s(r)$ and Fermi wave vector $k_F(r)$ by

$$\tfrac{4}{3}\pi[r_s(r)a_0]^3\ \rho(r)=1 \tag{B1}$$

and

$$k_F^3(r)/3\pi^2=\rho(r). \tag{B2}$$

Then the wave functions and energies appropriate to ground-state properties are given by the (self-consistent) solution of the equations (in atomic units):

$$[-\nabla^2+V_H(r)+\mu_{xc}(r)]\psi_i(r)=E_i\psi_i(r)\ , \tag{B3a}$$

$$\rho(r)=\sum_{\text{occupied}}|\psi_i(r)|^2\ . \tag{B3b}$$

Here V_H is the Hartree potential due to core and conduction electrons. The remaining exchange-correlation part of the potential $\mu_{xc}(r)$ has been the object of considerable theoretical activity. We have used the results given in Hedin and Lundqvist.[3] In particular

$$\mu_{xc}(r_s(r))=\beta(r_s)\mu_x(r_s)\ , \tag{B4}$$

where

$$\mu_x(r_s)=-(e^2/\pi)(3\pi^2\rho)^{1/2} \tag{B5}$$

and $\beta(r)$ is given in Fig. 1 of Ref. 3. Alternately β is approximated by the analytic formula

$$\beta(r_s)=1+0.7734\ln(1+1/x)\ , \tag{B6}$$

where $x=\frac{1}{21}r_s$. The ground-state calculation must be completed before computing the excitation potential, for which $\rho(r)$ is a necessary ingredient.

Excitation potential

To calculate energy levels appropriate to excitation processes, such as optical absorption or photoemission, we use a result from many body theory (see, for example, the discussion in Refs. 1–3) that the excitation energies E_k are the self-consistent solutions of the equations

$$[-\nabla^2+V_H(r)+V_{xc}(r)]\phi_k(r)=E_k\phi_k(r) \tag{B7a}$$

$$V_{xc}(p,r)+p^2=E_k+\mu_n(r)\ . \tag{B7b}$$

Here V_H is the Hartree potential resulting from the self-consistent solution of (B3), and the local chemical potential is

$$\mu_n(r)=k_F^2(r)+\mu_{xc}(r). \tag{B8}$$

The sticky point is that the exchange-correlation excitation potential $V_{xc}(p,r)$ is a function of the excitation energy E_k via the local momentum p. Hence one requires a tabulation of V_{xc} as a function of both $r_s(r)$ and $p/k_F(r)$. (Given in Table 2 of Ref. 3.) Unfortunately the calculations for this are not nearly so sophisticated as those for $\mu_{xc}(r_s)$ and it can easily occur in the computation that the Fermi level depends on r, for example. To avoid these physical incongruities we replace V_{xc} in Table 2 of Ref. 3 by

$$V_{xc}-\mu_{xc}(r)\left(\frac{V_{xc}(p,r)}{V_{xc}(k_F,r)}\right)\ , \tag{B9}$$

as already suggested in Ref. 3. Unfortunately this point seems to have been overlooked in other calculations using the excitation potential.[2,5,15]

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[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964); W. Kohn and L. Sham, Phys. Rev. 140, A1333 (1965); L. Sham and W. Kohn, Phys. Rev. 145, 561 (1966).

[2] For a recent discussion of these points, see the review article of U. von Barth and L. Hedin, Nuovo Cimento B, 23, 1 (1974).

[3] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[4] K. S. Singwi, A. Sjölander, M. P. Tosi, and R. H.

Land, Phys. Rev. B 1, 1044 (1970).

[5] There have been efforts to calculate the effects of the excitation potential: L. Dagens and F. Perrot, Phys. Rev. B 8, 1281 (1973) (for Li, Na, and K); G. Arbman and U. von Barth, Nuovo Cimento B 23, 37 (1974); and (unpublished) (for Al). To be fair, the difference between the ground-state and excitation potentials is usually quite small, as is pointed out in Ref. 2.

[6] H. Ehrenreich and L. Hodges, Methods Comput. Phys. 8, 149 (1968).

[7] X_1 is often cited as the bottom of the *d* bands; however, it is heavily hybridized with the non-*d* electrons with a resultant depression of its energy. We concentrate instead on the lowest-lying pure-*d*-like state, which is X_3, and may as a result slightly underestimate the conventional *d*-band width.

[8] L. Hodges, R. E. Watson and H. Ehrenreich, Phys. Rev. B 5, 3953 (1972). The renormalized atom is applied to the 3*d* and 4*d* transition metals. The values for Ni may be gleaned from Fig. 4, although we actually use ϵ_Γ^{WS} from Fig. 5. In addition the *d*-band width is available in Fig. 8 ($d^{n-1}s$).

[9] Fully discussed in Ref. 8. For its application to rare-earth metals, see J. F. Herbst, D. N. Lowy, and R. E. Watson, Phys. Rev. B 6, 1913 (1972). In J. F. Herbst and R. E. Watson, Phys. Rev. Lett. 34, 1395 (1975) summary results on the actinide metals are available.

[10] C. D. Gelatt, R. E. Watson, H. Ehrenreich, and L. Hodges (unpublished).

[11] For example, S. Hüfner, G. K. Wertheim, N. V. Smith, and M. M. Traum, Solid State Commun. 11, 323 (1972); and D. E. Eastman, in *Electron Spectroscopy*, edited by D. A. Shirley (American Elsevier, New York, 1972).

[12] John W. D. Connolly, Phys. Rev. 159, 415 (1967); (20 nonequivalent $\vec{k}$-space points used in calculation).

[13] J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973); (energy levels computed at 505 points in $\frac{1}{48}$ of the Brillouin zone).

[14] N. D. Lang and W. Kohn, Phys. Rev. B 3, 1215 (1971); 8, 6010 (1973).

[15] J. F. Janak, A. R. Williams, and V. L. Moruzzi, Phys. Rev. B 6, 4367 (1972); and (private communication).

[16] B. Y. Tong, Phys. Rev. B 6, 1189 (1972).

[17] W. Y. Ching and J. Callaway, Phys. Rev. B 9, 5115 (1974).

[18] R. E. Watson and H. Ehrenreich, Comments Solid State Phys. III, 109 (1970).

[19] G. G. Scott and R. A. Reck, Phys. Rev. B 8, 223 (1973).

[20] Descriptions and graphs of the energy and density dependence of the excitation potential are given in Ref. 3.

[21] W. D. Grobman and D. E. Eastman, Phys. Rev. Lett. 33, 1034 (1974).

[22] O. K. Andersen, Solid State Commun. 13, 133 (1973).