RENORMALIZED ATOMS AND THE BAND STRUCTURE OF TRANSITION METALS*

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A microscopic interpretation of ϵ_d, the mean d-band energy in the Heine-Hubbard interpolation description of the transition metals, and of $\epsilon(\Gamma_1)$, the bottom of the conduction bands, is given in terms of a "renormalized atom" concept. The implication for the cohesive energy of the transition metals is considered within the same framework and contrasted to the alkali metals.

The noble and transition metal electron band structures are largely determined by two parameters[1]: first, the width w of the d band which is related to the lifetime h/w of the virtual d state at a given site; and second, the energy ϵ_d of the center of gravity of the d bands. This specifies the d-band position with respect to $\epsilon(\Gamma_1)$, the bottom of the s-p conduction bands. In addition, there are also effects associated with the lattice structure. It is clear, however, particularly from a Kohn-Rostoker[2] point of view, that these are computationally innocuous in that they may be tabulated once and for all in the form of structure constants. They will be of no concern here. Heine, Hubbard, and others[1] have explored how all of these, as well as d-band–conduction-electron hybridization (which is closely related to w), affect the band structure. While it has been clear how to calculate w in terms of atomic quantities, a corresponding satisfactory description of ϵ_d on the basis of atomic considerations has been lacking. This note will show how ϵ_d may be estimated from atomic considerations and in particular that it differs appreciably from the free-atom d level obtained at infinite atomic separations with which it has been frequently associated.[3] These same atomic considerations can be used to infer $\epsilon(\Gamma_1)$.

Contrary to most present band-potential constructs, which are based on overlapping atomic charge densities, the present approach focuses on a "renormalized atom" description for which l-dependent Hartree-Fock crystal potentials may be derived.[4] This was first used by Chodorow, and subsequently by Segall for Cu.[5] It involves lopping off the free-atom s- and d-wave functions at the Wigner-Seitz radius, r_{WS}, and renormalizing them to the Wigner-Seitz sphere. This procedure preserves the shape of the functions inside the sphere. We will consider the face-centered cubic transition metals assumed in a $d^n s^1$ configuration,[6] which is that most nearly appropriate for band calculations. For these, the renormalization increases the d charge inside the sphere by less than 5%, but increases the s charge by a factor of 2 to 3. This large compression of the s charge towards the ion core is primarily responsible for the cohesive energy of the (bcc) alkali metals[7] (as can be seen for the example of K given in Table I). On compression, the s electron interacts more strongly with the interior electrons but this repulsion is outweighed by the increased nuclear attraction. (An additional contribution to the binding arises from the Wigner-Seitz boundary conditions which serve to reduce the kinetic energy.[8]) The increased s-d (and d-d) interactions in the transition metals make the nuclear attraction of d electrons less effective. As can be seen from the table, this causes an increase of approximately 0.5 Ry in ϵ_d from its free-atom value. This shift is nearly constant for the atoms considered here. As will be shown, this surprisingly large increase does not adversely affect the binding energy of the renormalized atom. Because of the large distortion of the s charge, it is less relevant to examine the renormalized s electron's one-electron energy than that of an orthogonalized plane wave (OPW), ϕ, at $k=0$ in the renormalized potential:

$$\epsilon(\Gamma_1) \equiv \int_{\text{WS sphere}} \phi^*(r)\left[-\tfrac{1}{2}\nabla^2 + V_{\text{ren}}^{\,l=0}\right]\phi(r)\,d\tau.$$

This represents an estimate of the conduction-band energy at Γ_1. The table compares the free-atom s energies $\epsilon(s)$ with $\epsilon(\Gamma_1)$ and with the value determined from a first-principles augmented plane wave calculation based on the l-dependent renormalized atom potential with its outer regions replaced by the standard muffin tin. $\epsilon(\Gamma_1)$ lies lower than the atomic $\epsilon(s)$ because of the in-

Table I. Energies in Ry.

		K	Co(d^8s)[a]	Ni(d^9s)	Cu($d^{10}s$)	Ag($d^{10}s$)
Free Atom	ε_d	---	-0.718	-0.797	-0.914	-1.037
Renormalized Atom	ε_d	---	-0.185	-0.278	-0.399	-0.625
Center of Gravity						
of Γ Levels		---	-0.183	-0.265	-0.400	-0.606
of X Levels		---	-0.199	-0.276	-0.410	-0.598
Free Atom	ε_s	-0.30	-0.43	-0.44	-0.46	-0.43
Renormalized Atom	$\varepsilon(\Gamma_1)$	-0.46	-0.75	-0.79	-0.83	-0.74
Band Calculation	$\varepsilon(\Gamma_1)$	---	-0.71	-0.76	-0.81	-0.72
ΔE, Energy Difference (Renormalized Atom Minus Free Atom)		-0.067	$+0.000_3$	-0.009	-0.035	-0.010
Experimental Binding Energy (Per Atom)		-0.069	-0.335	-0.322	-0.258	-0.220

[a] Evaluated for the average of the d^8s configuration.

creased potential energy and the change in kinetic energy associated with the Wigner-Seitz boundary conditions. Despite the perturbation theoretic nature of our estimates and the muffin-tin approximation used in these band calculations, the renormalized atom estimates of $\epsilon(\Gamma_1)$ are seen to be in good agreement with the energy band results.

The same band calculations can be used to infer the relationship between ϵ_d, obtained for a renormalized *d* function in the renormalized atom potential, and those of the *d* bands. The table shows that the center of gravity of the *d*-band levels at Γ and *X*, defined as $\frac{3}{5}\epsilon(\Gamma_{25'}) + \frac{2}{5}\epsilon(\Gamma_{12})$ and as $\frac{1}{5}\epsilon(X_1)+\frac{1}{5}\epsilon(X_3)+\frac{1}{5}\epsilon(X_2)+\frac{2}{5}\epsilon(X_5)$, respectively, differ by less than 0.03 Ry from the renormalized atom values for ϵ_d. This, together with the successful estimate of $\epsilon(\Gamma_1)$, shows the usefulness of the renormalized atom concept in providing resonant *d* levels, about which the *d* bands may be said to broaden, as well as their position relative to the conduction bands. Furthermore, it is this ϵ_d which should be used as a starting point for cohesive energy estimates of the type given by Cyrot[9] and Friedel.[3] In fact, their approach is reasonable only if the constancy of the renormalization shift already noted for Co, Ni, and Cu holds for the entire third row, particularly since these shifts are comparable with the *d*-band width.

The agreement of the renormalized atom estimate of the resonant *d* level with the center of gravity of the bands may be surprising in view of the strong variation in crystal *d*-wave function character in passing from the bottom to the top of the bands. However, as has been known since the first transition metal atom calculation of the Hartrees, and as will be discussed in a subsequent paper, a *d*-level energy is insensitive to the exact shape of the radial wave function. This fact provides some justification for the use of energy-independent pseudo *d*-wave functions in the interpolation schemes of Mueller and Hodges.[10]

Despite the large renormalization shifts of ϵ_d, the total Hartree-Fock energy *E* of the free and renormalized atoms is almost identical. This is because the electron-electron Coulomb, U_{ij}, and exchange, J_{ij}, terms which are responsible for the renormalization shifts do not have equal weight in the total energy, i.e.,

$$E = \sum_i \{\epsilon_i - \tfrac{1}{2} \sum_j [U_{ij} - J_{ij}\delta(m_{si} m_{sj})]\},$$

where the sums are over occupied states. The subtraction removes electron-electron terms which would otherwise be erroneously doubly counted in the sum over i. Volume renormalization of the Coulomb terms in this equation virtually cancels the shifts associated with ϵ_i. The small change in E occurs either for the atom with a renormalized atomic s electron or for an atom with an OPW corresponding to $k = 0$ plus the added kinetic energy associated with occupying a free-electron conduction band. The energy differences ΔE of the latter with respect to the free atoms, which are given in the table, are very small indeed compared with the total energy of an atom (~3000 Ry for Cu). ΔE is smaller in the transition metals than in the alkalis and thus plays essentially no role in transition metal[11] binding. Therefore, effects like s-d hybridization in the noble metals, and additional effects due to the partial occupation of the broadened d bands in the transition metals,[9] play an even greater role in the cohesive energies than is traditionally thought.

Renormalized atom estimates of the bandwidth and hybridization parameters entering the Heine-Hubbard theory[1] are also in good accord with the band calculations. These and further details will be described in a later publication.

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Note added in proof.—Self-consistent-field estimates of the atomic d^ns configurations suggest somewhat larger ΔE for the noble metals and behavior of the sort reported above for the transition elements.

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[1] V. Heine, Phys. Rev. 153, 673 (1967); J. Hubbard, Proc. Phys. Soc. (London) 92, 921 (1967); J. Hubbard and N. W. Dalton, J. Phys. C: Proc. Phys. Soc., London 1, 1637 (1968).

[2] E.g., B. Segall and F. Ham, Methods Comput. Phys. 8, 251 (1968).

[3] J. Friedel, in *Theory of Magnetism in Transition Metals, Proceedings of the International School of Physics "Enrico Fermi," Course XXXVII*, edited by W. Marshall (Academic, New York, 1967), p. 283.

[4] This description possesses the feature that exchange is included explicitly, as in atomic calculations, without resort to the $\rho^{1/3}$ approximation. The k dependence of the exchange interaction in the present treatment is not handled rigorously, but this dependence is unimportant for all but conduction electron-conduction electron terms. It should also be noted that correlation effects can be and are included to the extent characteristic of Wigner-Seitz calculations (i.e., a full self-Coulomb hole is always present at the site in question).

[5] M. Chodorow, Phys. Rev. 55, 675 (1939); B. Segall, Phys. Rev. 125, 109 (1962).

[6] For lack of d^ns neutral-atom wave functions, we have used monovalent d^n ion wave functions with s orbitals added. This suffices for our present purposes.

[7] E. P. Wigner and F. Seitz, Solid State Phys. 1, 97 (1955).

[8] Of course, in a rigorous description, the potential and kinetic energy terms vary together as is required by the virial theorem.

[9] F. Cyrot-Lackmann, J. Phys. Chem. Solids 29, 1235 (1968).

[10] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966); F. M. Mueller, Phys. Rev. 153, 659 (1967).

[11] Preliminary results suggest that ΔE may be positive and of the order of 0.1 Ry for the lighter bcc transition metals.