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Simple model of multiple charge states of transition-metal impurities in semiconductors

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The Anderson model for magnetic impurities in metals is extended to semiconductors. It is shown how self-consistent Hartree-Fock solutions can exist in the gap for many different charge states of the impurity, providing the matrix elements coupling the impurity and substrate are large enough.

INTRODUCTION

In contrast to the shallow hydrogenic impurity states resulting from doping semiconductors with impurity atoms having similar pseudopotentials to their host, doping with transition metals gives rise to a remarkable sequence of levels deep in the gap, corresponding to often as many as five different charge states of the impurity. (See, for example, Ref. 1 for a chart of such impurity levels.)

Spin resonance studies[2] show that the electronic configuration of the impurity atom can be chosen to be compatible with measures S, J values by a simple phenomenological model: in substitutional impurities, enough d electrons to satisfy bonding requirements are promoted to sp^3 orbitals; in interstitials, all valence electrons go into d orbitals. The occupation of the d states then varies as electrons are accepted or donated. The ESR studies indicate considerable hybridization between the d orbitals of the impurity and the band states of the substrate semiconductor.

In view of the fact that the energies separating different charge states of the free atom are of the order of tens of volts, it seems remarkable, even allowing for dielectric screening, that such different charge states as, for example, Au^{3-} and Au^{+} can occur in the 0.8-eV gap of germanium. The key to the understanding of these states lies in the hybridization which allows the nominal occupancy of d-like states to vary considerably, while keeping the actual amount of charge in the core regions of the transition-metal atom almost the same as in the free atom.

We have developed a simple model which shows how the impurity can bind many electrons or holes without this actual charge on the impurity atom itself changing by more than a fractional amount.

I. MODEL HAMILTONIAN

The magnetic properties of transition-metal impurities in nonmagnetic metals are usually understood by means of the Anderson Hamiltonian[3,4] (We use a simplified version of the usual Hamiltonian here, only keeping the dominant Coulomb term U in the two-particle part, and omitting the exchange term J.)

$$H = E_d \sum_{m\sigma} n_{m\sigma} + \tfrac{1}{2} U \sum_{m\sigma \neq m'\sigma'}{}' n_{m\sigma} n_{m'\sigma'} + \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{km\sigma} V_{mk} c^{\dagger}_{m\sigma} c_{k\sigma} + V_{km} c^{\dagger}_{k\sigma} c_{m\sigma} . \qquad (1)$$

We will use it, suitably reinterpreted, to investigate the properties of these impurities in semiconductors.

The ϵ_k and $n_{k\sigma}$ are the energies and occupancies of free-electron-like states of the substrate semiconductor. In a metallic model, this density of states is usually taken to be constant; to model a semiconductor, we have introduced a gap. For simplicity, the matrix elements V_{mk} were taken to be independent of m and k. E_d and $n_{m\sigma}$ refer to a set of localized orbitals on the same site, for example, the 10 nearly degenerate orbitals $|m\sigma\rangle$ of Mn on a cubic impurity site. U is the strong intra-atomic Coulomb repulsion between electrons localized in d orbitals in the core of the atom.

The main omission in (1) is the Coulomb interaction between electrons in $|k\rangle$ states, and in $|k\rangle$ and $|d\rangle$ states. This can partly be allowed for by reducing U, and treating it as a net *extra* repulsion between electrons in the very localized d states. This, however, still fails to treat the long-range part of the Coulomb interaction due to a net charge localized in the surroundings of the impurity. This will only have appreciable effect on highly charged, weakly bound states of the impurity, as energies associated with this long-range force are of the order of $(\text{charge})^2$ times the appropriate rydberg for the semiconductor.

Other omissions such as the exchange energies, and differences in U for interactions between electrons in different m states, which determine the actual state LSJ of the free atom, only affect details, and could be included as perturbations.

To model the band structure, we chose a constant density of k states ρ_k with a gap between the valence- and conduction-band edges at ϵ_v and ϵ_c. These sharp band edges guarantee a pole in the final density of states in the gap for each of the 10 $m\sigma$ values.

The impurity atom is characterized by the parameters E_d and U, the semiconductor by the gap width $\epsilon_c - \epsilon_v$, and the interaction between k and d states by the quantity $\Delta = \pi |V_{kd}|^2 \rho_k$; together, these four energies completely determine the model.

The model has been solved in the Hartree-Fock approximation, for a series of states with different numbers of the 10 poles in the gap occupied, and a range of different values of the four energies describing the atom, semiconductor, and interaction. Whether states corresponding to donor and acceptor levels were bound, and at what energy, was determined by examining the differences in the *total* energy of solutions with different numbers of electrons; since the amount of hybridization changes a great deal as occupancy changes, Koopmans theorem is inappropriate here.

Over a large range of the parameters, multiply charged states in the gap were found.

II. DETAILS OF METHOD USED TO SOLVE HAMILTONIAN

A. General

The Hamiltonian was solved in the unrestricted Hartree-Fock approximation (HFA), using a Green's-function method. First, a single-particle effective Hamiltonian was solved in terms of the parameter $E^{\text{eff}}_{m\sigma}$:

$$H^{\text{eff}}_{m\sigma} = E^{\text{eff}}_{m\sigma} n_{m\sigma} + \sum_k \epsilon_k n_{k\sigma} + \sum_k V_{kd} c^\dagger_{k\sigma} c_{m\sigma} + \text{c.c.} \quad (2)$$

The parameters $E^{\text{eff}}_{m\sigma}$ must be determined self-consistently from

$$E^{\text{eff}}_{m\sigma} = E_d + U \sum_{m\sigma \neq m'\sigma'}{}' \langle n_{m'\sigma'} \rangle \,. \quad (3)$$

$\langle n_{m\sigma} \rangle$ was calculated from (2) using

$$\langle n_{m\sigma} \rangle = \frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{E_F} G_{m\sigma}(\omega)\, d\omega \,, \quad (4)$$

where (see Appendix A)

$$G_{m\sigma}(\omega) = [\omega - E^{\text{eff}}_{m\sigma} - \Sigma(\omega)]^{-1} \,, \quad (5)$$

$$\Sigma(\omega) = \sum_k \frac{|V_{kd}|^2}{\omega - \epsilon_k} \,. \quad (6)$$

$\langle n_{m\sigma} \rangle$ was broken down into two contributions:

$$Z_1(E^{\text{eff}}_{m\sigma}) = \frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{\epsilon_v} G_{m\sigma}(\omega)\, d\omega \,, \quad (7)$$

$$Z(E^{\text{eff}}_{m\sigma}) = \frac{1}{\pi} \operatorname{Im} \int_{\epsilon_v}^{\epsilon_c} G_{m\sigma}(\omega)\, d\omega \,, \quad (8)$$

where Z_1 was the contribution to $\langle n_{m\sigma} \rangle$ from hybridization between d states and states of the occupied valence band, and Z was the residue of the pole of $G_{m\sigma}(\omega)$ in the gap, which might or might not be occupied, depending on ϵ_F.

Self-consistent solutions with different occupancies of the ten poles in the gap were found, and their *total* energies evaluated in the HFA. In Hartree-Fock, summing the single-particle energies double counts the two-particle terms, so we must subtract one half of these from the sum to get the total energy of the system in the HFA. The single-particle energy was further broken down into two parts: the band-structure energy contribution from the occupied orbitals of the valence band, and the energies of occupied poles in the gap at $\omega_p^{m\sigma}$, where

$$\omega_p^{m\sigma} - \Sigma(\omega_p^{m\sigma}) - E^{\text{eff}}_{m\sigma} = 0 \,. \quad (9)$$

The total energy is

$$E^{\text{tot}} = \frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{\epsilon_v} \omega \operatorname{Tr} G(\omega)\, d\omega + \sum_{m\sigma \text{ occupied}} \omega_p^{m\sigma} - \tfrac{1}{2} U \sum_{m\sigma \neq m'\sigma'}{}' \langle n_{m\sigma} \rangle \langle n_{m'\sigma'} \rangle \,. \quad (10)$$

Since we are only interested in *changes* in the total energy as we add electrons to the system (and also as in our simple infinite-bands-with-a-gap model, the band-structure energy is infinite), we need only examine how the band-structure energy changes with the $E^{\text{eff}}_{m\sigma}$. From Appendix A we see that

$$\operatorname{Tr} G = \operatorname{Tr} G^0 + \sum_{m\sigma} \frac{d}{d\omega} \ln[\omega - E^{\text{eff}}_{m\sigma} - \Sigma(\omega)] \,, \quad (11)$$

where $G^0(\omega)$ is the Green's function for the pure semiconductor. Hence

$$\begin{aligned} \frac{\partial E^{\text{band}}}{\partial E^{\text{eff}}_{m\sigma}} &= \frac{-1}{\pi} \operatorname{Im} \int_{-\infty}^{\epsilon_v} \omega \frac{d}{d\omega} [\omega - E^{\text{eff}}_{m\sigma} - \Sigma(\omega)]^{-1} \\ &= \frac{-1}{\pi} [\operatorname{Im} \omega G_{m\sigma}(\omega)]_{-\infty}^{\epsilon_v} + \frac{1}{\pi} \operatorname{Im} \int_{-\infty}^{\epsilon_v} G_{m\sigma}(\omega)\, d\omega \\ &= Z_1(E^{\text{eff}}_{m\sigma}) \,. \end{aligned} \quad (12)$$

Thus we arrive at

$$E^{\text{tot}} = \sum_{m\sigma} \int^{E^{\text{eff}}_{m\sigma}} Z_1(E)\, dE + \sum_{m\sigma \text{ occupied}} \omega_p^{m\sigma} - \tfrac{1}{2} U \sum_{m\sigma \neq m'\sigma'} \langle n_{m\sigma} \rangle \langle n_{m'\sigma'} \rangle + \text{const.} \quad (13)$$

Given the set of $E^{\text{eff}}_{m\sigma}$, it is now trivial to evaluate the relative total energies for different self-consistent solutions.

B. Particular details of our model

The solutions we looked for were simple in form, and certainly unique in the nonmagnetic region (see later); n_v of the 10 $m\sigma$ states had a degenerate, occupied pole in the gap, and the other $(10-n_v)$ had a degenerate, unoccupied pole in the gap above the first one. (See Fig. 1.) In this case, (3) takes on a particularly simple form

$$x = E_d + U\{(n_v - 1)[Z_1(x) + Z(x)] + (10 - n_v)Z_1(y)\}, \quad (14)$$

$$y = E_d + U\{n_v[Z_1(x) + Z(x)] + (9 - n_v)Z_1(y)\}, \quad (15)$$

where x and y are the values of $E^{\text{eff}}_{m\sigma}$ for the states with occupied and unoccupied poles in the gap. $Z_1(\omega)$ and $Z(\omega)$ were tabulated, and are the characteristic functions of the problem. Equations (14) and (15) can be transformed from implicit to explicit form

$$y = x + \{E_d + 9U[Z_1(x) + Z(x)]\}/(10 - n_v), \quad (16)$$

$$x = y + [E_d + 9UZ_1(y)]/n_v. \quad (17)$$

These equations are easily solved, subject to the condition $x<y<x+U$ for physical solutions. In every case a unique self-consistent solution was found.

In our model, $\Sigma(\omega)$ becomes (see Fig. 2.)

$$\Sigma(\omega) = \frac{\Delta}{\pi}\ln\left(\frac{\omega - \epsilon_c}{\epsilon_v - \omega}\right), \quad (18)$$

where (ρ_k is the constant density of states in the semiconductor bands)

$$\Delta = \pi |V_{kd}|^2 \rho_k. \quad (19)$$

We write $\Sigma(\omega)$ as $\Sigma'(\omega) + i\Delta(\omega)$, where

$$\Sigma'(\omega) = \frac{\Delta}{\pi}\ln\left|\frac{\omega - \epsilon_c}{\omega - \epsilon_v}\right|,$$
$$\Delta(\omega) = \begin{cases} \Delta\ \omega < \epsilon_v, & \omega > \epsilon_c, \\ 0, & \epsilon_v < \omega < \epsilon_c. \end{cases} \quad (20)$$

Then $Z_1(E^{\text{eff}}_{m\sigma})$ and $Z(E^{\text{eff}}_{m\sigma})$, which must be calculated numerically and tabulated, are given by

$$Z_1(E^{\text{eff}}_{m\sigma}) = \frac{1}{\pi}\int_{-\infty}^{\epsilon_v} \frac{\Delta}{[\omega - E^{\text{eff}}_{m\sigma} - \Sigma'(\omega)]^2 + \Delta^2}\,d\omega \quad (21)$$

and, since in the gap the integrand becomes a δ function at $\omega_p^{m\sigma}$ with strength Z,

$$Z(E^{\text{eff}}_{m\sigma}) = \left|1 - \frac{d}{d\omega}\Sigma'(\omega)\right|^{-1}_{\omega_p^{m\sigma}}, \quad (22)$$

where $\omega_p^{m\sigma}$ is the position of the pole in the gap, given by (9) (see Fig. 3).

III. RESULTS OF CALCULATION

The types of solution of (2) and (3) for various values of the parameters describing the problem fall into two regimes, according to a criterion similar to that deciding between magnetic and nonmagnetic solutions in the problem of local moments on impurities in metals.

For $\Delta < U/\pi$, the weak coupling limit, the ground state of the impurity resembles the free atom, with at best one or two bound levels in the gap appearing as Δ increases. The total energy of self-consistent solutions of (3), as a function of the number of bound electrons n_v has a pronounced minimum near the valency of the neutral free atom (Fig. 4). As Δ approaches the transition region $\Delta \sim U/\pi$, this minimum disappears (Fig. 4) and all ten possible charge states of the impurity can be bound in the gap by varying the Fermi level (Fig. 5). As Δ becomes the dominant term in the three energies (U, Δ, gap width) characterizing the problem, the levels in the gap become a 10-degenerate level repelled to the gap center by the band edges. In this limit many-electron effects on the impurity atom become negligible, since Z, the fraction of atomic d orbital in the localized gap-state wave functions goes to zero. The dominant Coulomb terms in this limit are the long-range

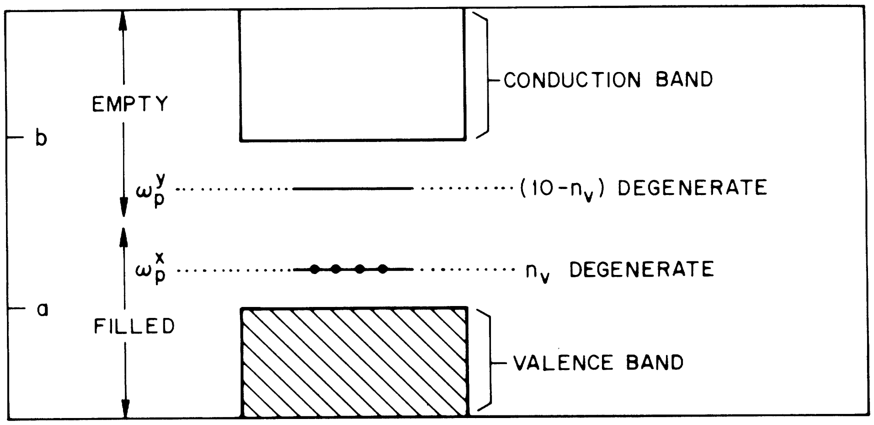

FIG. 1. Type of Hartree-Fock solution looked for.

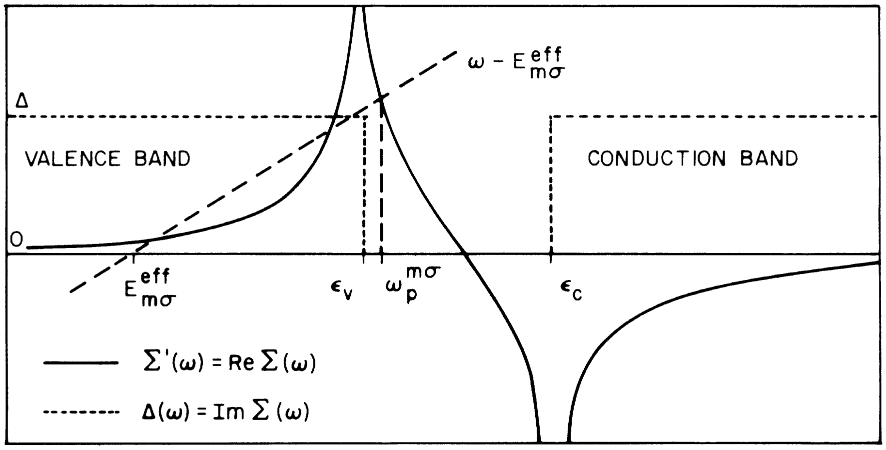

FIG. 2. Self-energy function $\Sigma(\omega)$ and position of pole in gap.

ones omitted in our model Hamiltonian, and the model clearly becomes unphysical in this extreme limit.

Examining the variation of the charge in the core regions of the atom, as occupancy n_v of d-like gap states changes (Fig. 6), we notice that the self-consistency requirement prevents this charge from varying by more than a fraction of an electron throughout the whole series of 10 levels.

This is the key to understanding how so many valence states are energetically available to the impurity. Adding an electron increases the charge by Z; this is compensated by an upward shift of the level of the pole of $G(\omega)$ in the gap, which reduces Z_1, the contribution to the d occupancy from hybridization with valence-band states, by exactly the right amount: whatever the valence, the charge on the impurity can remain close to neutrality. The extra charge is localized in the long hydrogenic tail regions of the impurity wave function.

The effect of changing U in the calculation is shown in Fig. 7. U is half of its value in the previous calculation (Fig. 5). (E_d is also halved to keep the atoms comparable.) The main difference in the results is that the transition value of Δ, U/π, is halved. The insensitivity of the strong coupling regime to U is apparent in the similarity of the results for $\Delta > U/\pi$: This reflects the increasing irrelevance of the intra-atomic two-electron term in this limit.

IV. DISCUSSION

The point we wish to demonstrate in this calculation is that localized systems where correlation and other many-electron effects are important, hybridizing with a substrate system of extended states, may have properties that can be described by the occupation of orbitals with a fraction Z of local character. The occupations of these orbitals can differ greatly from those we expect intuitively from charge neutrality, etc.

Our model leaves out many features, notably exchange interactions (filling of d levels in the experimental results of Ref. 4 is in accordance with Hunds rules—spin is maximized), and symmetry effects (d levels split into T_2 and E branches in

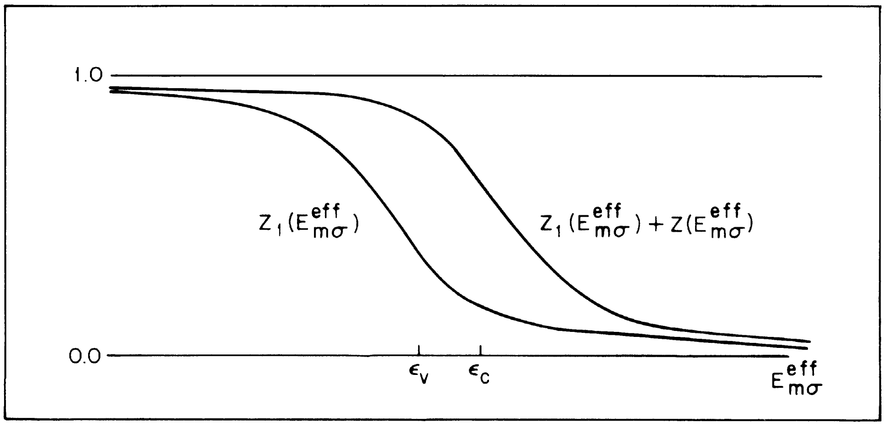

FIG. 3. Typical form of $Z_1(E^{eff}_{m\sigma})$ and $Z_1(E^{eff}_{m\sigma}) + Z(E^{eff}_{m\sigma})$.

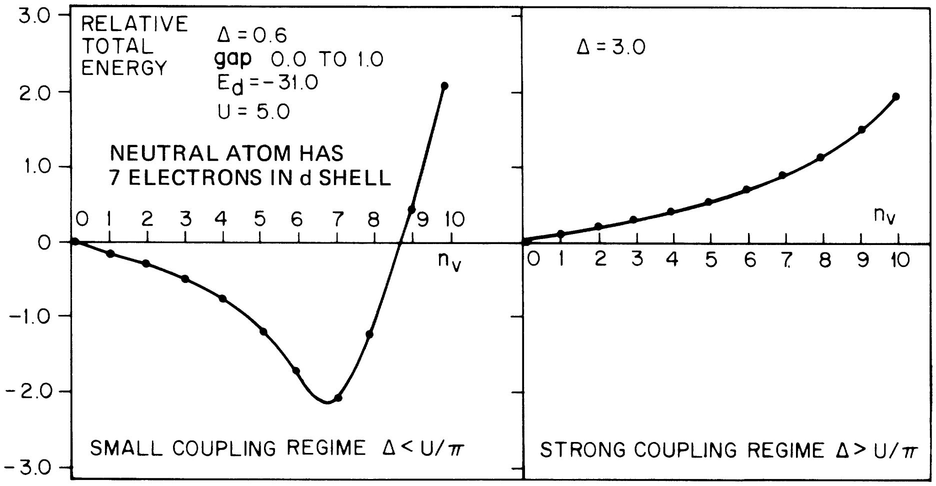

FIG. 4. Total energy of self-consistent solutions (3) as number of bound electrons (n_v) is increased.

cubic symmetry: only T_2 symmetry states couple to the valence band in diamond-structure semiconductors).

Only the omitted long-range Coulomb effects will involve effective masses and details of the band structure, which are not important in treating effects of self-consistency on the central atom (modifying the square edged density of states with a quadratic termination has little effect on the results of this calculation).

We expect our model to be reasonable physically in the region of Δ around U/π or smaller. For example, substitutional gold will have seven *d* electrons in its neutral state: Figs. 5 or 6 compare reasonably with gold in germanium, (Ref. 1) for Δ in the transition region.

We expect that these ideas on the importance of treating interacting local and extended systems self-consistently may also be applied to such problems as the states of molecules adsorbed on catalytic surfaces, transition-metal ions in enzymes, etc.

APPENDIX A: GREEN'S FUNCTIONS FOR ANDERSON HAMILTONIAN

$$H=\sum_k \epsilon_k n_k + \sum_m E_m n_m + \sum_{k,m} V_{km} c_k^\dagger c_m + V_{mk} c_m^\dagger c_k \ ;$$

single-particle effective Anderson Hamiltonian (spin indices suppressed). From $(\omega - H)G = I$, we obtain

$$(\omega-\epsilon_k)G_{kk'} - \sum_m V_{km} G_{mk'} = \delta_{kk'} \ , \qquad \text{(A1)}$$

$$(\omega-\epsilon_k)G_{km} - \sum_{m'} V_{km'} G_{m'm} = 0 \ , \qquad \text{(A2)}$$

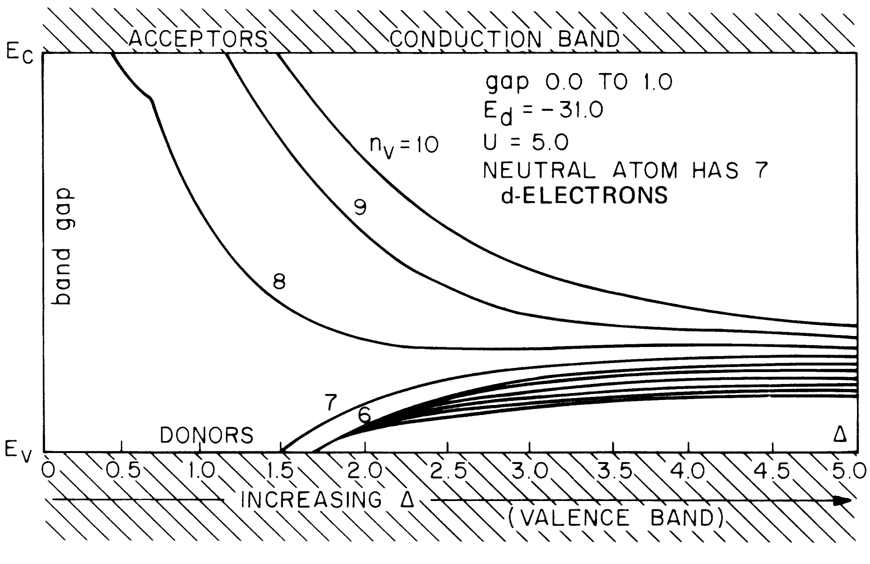

FIG. 5. Bound states in the gap for a given model atom and semiconductor as a function of Δ.

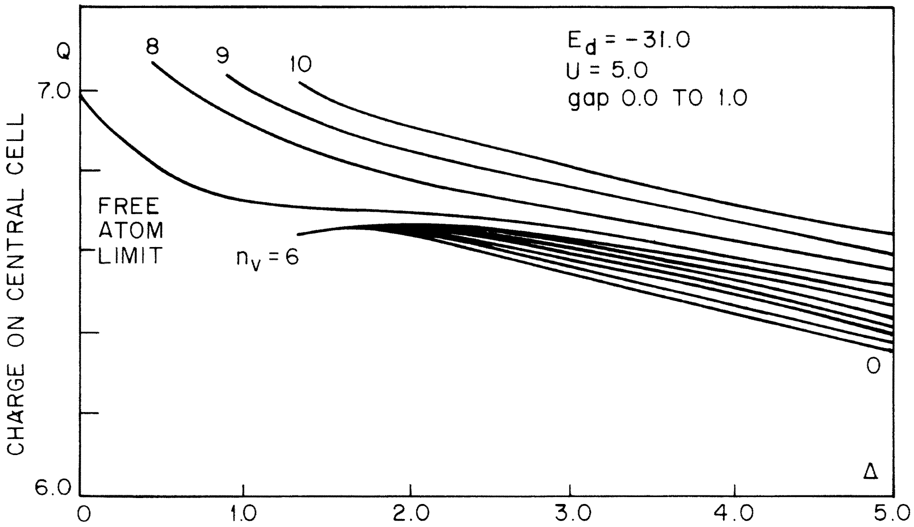

FIG. 6. Variation of Q, the total charge in the d-orbitals, with Δ for given atom, semiconductor.

$$(\omega - E_m)G_{mk} - \sum_{k'} V_{mk'}G_{k'k} = 0 \ , \qquad \text{(A3)}$$

$$(\omega - E_m)G_{mm'} - \sum_{k} V_{mk}G_{km'} = \delta_{mm'} \ . \qquad \text{(A4)}$$

Using (A2) and (A4), we get

$$(\omega - E_m)G_{mm'} - \sum_{m''}\left(\sum_{k} \frac{V_{mk}V_{km''}}{\omega - \epsilon_k}\right)G_{m''m'} = \delta_{mm'} . \qquad \text{(A5)}$$

Now, on symmetry grounds[5]

$$\sum_{k} \frac{V_{mk}V_{km'}}{\omega - \epsilon_k} = \Sigma_m(\omega)\delta_{mm'} \ , \qquad \text{(A6)}$$

and (e) becomes

$$G_{mm'} = \delta_{mm'}[\omega - E_m - \Sigma(\omega)]^{-1} \ . \qquad \text{(A7)}$$

Using this in (A1)–(A3) we get the other elements of G:

$$G_{mk} = [V_{mk}/(\omega - \epsilon_k)]G_{mm} \qquad \text{(A8)}$$

and

$$G_{kk'} = \frac{\delta_{kk'}}{\omega - \epsilon_k} + \sum_{m} \frac{V_{km}V_{mk'}}{(\omega - \epsilon_k)(\omega - \epsilon_{k'})} G_{mm} \ . \qquad \text{(A9)}$$

Evaluating the trace of G,

$$\begin{aligned} \mathrm{Tr}G &= \sum_{m} G_{mm} + \sum_{k} G_{kk} \\ &= \sum_{k} \frac{1}{(\omega - e_k)} + \sum_{m}\left(1 + \sum_{k} \frac{|V_{mk}|^2}{(\omega - e_k)^2}\right)G_{mm} \\ &= \mathrm{Tr}G^0 + \sum_{m}\left(1 - \frac{d}{d\omega}\Sigma_m\right)(\omega - E_m - \Sigma_m)^{-1} \\ &= \mathrm{Tr}G^0 + \sum_{m} \frac{d}{d\omega} \ln[\omega - E_m - \Sigma_m(\omega)] \ . \qquad \text{(A10)} \end{aligned}$$

G^0 is the Green's function for the system without the impurity atom. $\Sigma_m(\omega)$ is a self-energy function for the impurity orbital $|m\rangle$.

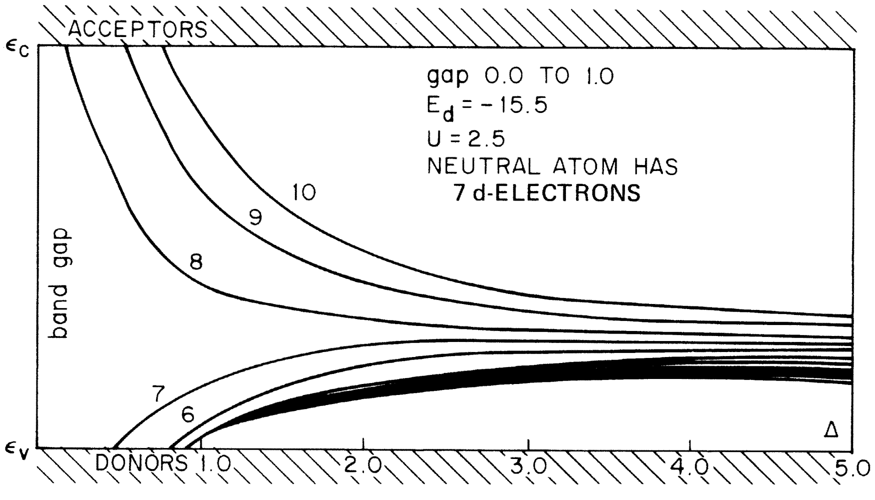

FIG. 7. Impurity level scheme when U is half of the value in Fig. 5.

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[3] P. W. Anderson, Phys. Rev. 124, 41 (1961).

[4] P. W. Anderson and W. L. McMillan, in *Proceedings of the International School of Physics "Enrico Fermi,"* XXXVII, The Varenna summer school, 1966, (Academic, New York, 1967), pp. 66, 67.

[5] The only symmetry not destroyed by the impurity atom is the point group about the impurity site. (Valid for an isolated impurity only.) Analyze each degenerate set of k states onto symmetry representations k^{α}: the m states are members of one representation of the point group, that is why they are degenerate, so each m corresponds to a different α:

$$\sum_k \frac{V_{mk}V_{km'}}{\omega-\epsilon_k} = \sum_{k,\alpha} \frac{\langle m\,|\,H\,|\,k\alpha\rangle\,\langle k\alpha\,|\,H\,|\,m'\rangle}{\omega-\epsilon_k}$$

$$= \sum_{k,\alpha} \frac{|\,\langle m\,|\,H\,|\,k\alpha\rangle\,|^2}{\omega-\epsilon_k}\,\delta_{mm'} \;.$$