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Separation of one- and many-electron effects in the excitation spectra of 3*d* impurities in semiconductors

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We present a new multiplet theory that separates mean-field from multiplet effects in the excitation and donor-acceptor ionization spectra of localized impurities. Analysis of the experimental data for all 3*d* impurities in ZnO, ZnS, ZnSe, and GaP for which sufficient data exist and for the bulk Mott insulators CoO, MnO, and NiO reveals, for the first time, regular chemical trends in many-electron effects with the impurity and the host-crystal covalency and delineates the regime where one-electron theory is applicable from the region where it is not.

Transition atom impurities in cubic semiconductors introduce gap levels of *e* and *t* symmetries and sustain a range of configurations[1,2] $e^m t^n$ through excitations $e^m t^n \rightarrow e^{m-1} t^{n+1}$ and ionizations from the valence band (VB), $(\mathrm{VB})^p t^n \rightarrow (\mathrm{VB})^{p-1} t^{n+1}$ (single acceptors) and to the conduction band (CB), $(\mathrm{CB})^0 t^n \rightarrow (\mathrm{CB})^1 t^{n-1}$ (single donors). The optical spectra[1,2] of these systems consist of sharp peaks which, like similar transitions in pure Mott insulators[3] (e.g., NiO, CoO) bear little resemblance to results of one-electron models.[3-7] Furthermore, the observed donor and acceptor ionization energies[1] show pronounced nonmonotonic trends with atomic number which are absent in mean-field electronic structure calculations.[5-7] Both phenomena have been known[3,8,9] to be related to many-electron multiplet effects. In mean-field (MF) calculations for systems with incomplete levels (N electrons in M-fold degenerate levels, with $N < M$), the one-body charge density is constructed by a procedure equivalent to assigning N/M of an electron to each of the M-fold degenerate partner levels. This projection produces a totally symmetric a_1 charge density and potential; each of the M degenerate eigenvalues has a common configuration-dependent energy term [the Racah parameter $A(m,n)$] reflecting interelectronic repulsions in this a_1-symmetric potential. Denoting by $\hat{H}_0$ the bare-ion Hamiltonian (i.e., that of a *single* unpaired electron ion, like Fe^{7+}) with its difference in diagonal elements $\Delta_{\mathrm{CF}} = \langle t|\hat{H}_0|t\rangle - \langle e|\hat{H}_0|e\rangle$ (the "crystal-field parameter"[8,9]), by $\hat{H}_1$ the interelectronic part, and by $\langle \hat{H}_1 \rangle$ its a_1-mean-field average, MF electronic structure calculations[4-7] produce eigenvalues and total energies $E_T(m,n)$ which are self-consistent solutions to $\hat{H}_0 + \langle \hat{H}_1 \rangle$, whereas the multiplet corrections (MC) left out correspond to $\hat{H}_1 - \langle \hat{H}_1 \rangle$. Existing multiplet approaches[7-10] have parametrized the $\hat{H}_0 + \hat{H}_1$ problem, often under severe approximations (such as[7-9] a single A for all configurations) and have consequently provided little insight into the relative importance of MC (the $\hat{H}_1 - \langle \hat{H}_1 \rangle$ problem) to MF electronic structure calculations (the $\hat{H}_0 + \langle \hat{H}_1 \rangle$ problem). In this paper we present a new approach to the multiplet problem which separates MF and MC effects. Its three central quantities—the effective crystal-field splitting Δ_{eff} and the orbital deformation parameters λ_e and λ_t—can be directly obtained from MF electronic structure calculations on impurities,[4-7] or, alternatively, they can be determined by fitting experiment. In the present work we determine them from the absorption spectra of all 3*d* impurities in ZnO, ZnS, ZnSe, and GaP for which sufficient data are available,[1,2] as well as for the bulk Mott insulators MnO, CoO, and NiO, establishing the extent of MC underlying the data. Our analysis isolates quantitatively the MC in excitation and ionization, revealing their regular chemical trends, removes hitherto unexplained contradictions between MF calculations and experiments, and predicts the energy of a few unobserved transitions.

Rather than distributing N electrons equally among all M patterns, spin and space unrestricted methods[8] distribute them in $\binom{M}{N}$ ways, yielding $\binom{M}{N}$ distinct Slater determinants. They allow thereby different electron orbits to get out of each other's way by occupying spacially distinct and variationally independent orbitals. New combination states (multiplets) result from diagonalizing $\hat{H}_0 + \hat{H}_1$ in this determinantal basis. The αth diagonal elements for representation Γ are[8]

$${}^{\Gamma}D_{\alpha\alpha}(m,n) = E^{\alpha}_{\mathrm{SC}}(m,n) + \Delta_{\mathrm{CF}}\ , \tag{1}$$

where the single-configuration (SC) energy $E^{\alpha}_{\mathrm{SC}}(m,n)$ represents a matrix element of $\hat{H}_1$ for a fixed configuration $e^m t^n$ of Γ, and Δ_{CF} is the one-electron crystal-field parameter of $\hat{H}_0$. $E^{\alpha}_{\mathrm{SC}}(m,n)$ includes the a_1-averaged interelectronic energy present in MF calculations as well as the anisotropic contribution of the two-electron (Slater-Condon) integrals which are not. The ten independent integrals can be collapsed into three parameters (the Racah parameters A, B, and C) if it is assumed that the e and t states share the same radial function and have a single ($l=2$) angular part. Alternatively, this approximation can be improved[7,10-12] by viewing the interelectronic integrals as the corresponding products of the free-ion integrals B_0 and C_0 and the orbital deformation parameters

$$\lambda_e^4 = \langle ee|\hat{H}_1|ee\rangle_{\mathrm{sol}} / \langle dd|\hat{H}_1|dd\rangle_{\mathrm{ion}}$$

and

$$\lambda_t^4 = \langle tt|\hat{H}_1|tt\rangle_{\mathrm{sol}} / \langle dd|\hat{H}_1|dd\rangle_{\mathrm{ion}}$$

(with[7,10] $\lambda_{et} = \sqrt{\lambda_e \lambda_t}$), representing ration between the interaction in the solid (sol) and the ion (ion). The off-diagonal elements of Eq. (1) represent configuration mixing and depend only on B_0, C_0, λ_e, and λ_t. The atomic (Racah's) limit corresponds to $\lambda_e = \lambda_t = 1$, and $\Delta_{\mathrm{CF}} = 0$; since $A(d^N)$ appears identically in $E^{\alpha}_{\mathrm{SC}}(N)$ for all $\binom{M}{N}$ terms it does not affect the multiplet splitting. Fitting the observed free-ion transitions produces the values[8] of B_0 and

C_0. In the classical crystal-field approach of Sugano, Tanabe, and Kamimura,[2,9] differential hybridization is ignored (hence $\lambda_e = \lambda_t$), and all e^m and t^n orbitals are assumed to be equally deformed in the anisotropic field (same A for all $e^m t^n$), and hence A is artificially dropped from the model. Fitting the impurity spectra produces B, C, and Δ_{CF}. In the Hemstreet-Dimmock (HD) approach,[7] it is assumed that a MF calculation for a *specified configuration* $e^m t^n$ includes the average multiplet effects of *all* configurations with $m+n=\mathrm{const}$, an internally inconsistent assumption. This results in the same $A=(14B-7C)/9$ for all configurations with $m+n=\mathrm{const}$. Instead, we assume that a mean-field calculation for $e^m t^n$ includes in it the average multiplet effects of just this configuration. This results in a different $A(m,n)$ for each configuration. We further show that the problem can be rigorously transformed in a way that the calculation of A in terms of B and C becomes unnecessary. These diverging assumptions (Refs. 2, 7–9 versus the present method) lead to distinctly different multiplet energies. The physical basis for this difference is that $A \gg B,C$; hence even small differences in A can alter dramatically the excitation spectra. Further, λ_e and λ_t are equated in the HD approach arbitrarily with the d orbital charge enclosed in a sphere of a selected radius for e and t orbitals, respectively (i.e., $1/r_{12}$ appearing in λ_e and λ_t is replaced by 1).

Our transformation is based on the ansatz that MF calculations for a given configuration $e^m t^n$ includes in its total energy $E_T(m,n)$ the average of the single configuration energies $E^g_{\mathrm{SC}}(m,n)$ of all multiplets that belong to this configuration. Defining the average single configuration energy as

$$\hat{E}(m,n)=\sum_i \omega_i E^i_{\mathrm{SC}}(m,n) \quad , \tag{2}$$

where the weights

$$\omega_{S,\Gamma}=(2S+1)g_\Gamma \Big/ \sum_{S,\Gamma}(2S+1)g_\Gamma$$

include both spin (S) and space (g_Γ) degeneracies, and expressing the *relative* multiplet shift induced by interelectronic interactions within a single configuration as

$$\Delta E^\alpha_{\mathrm{SC}}(m,n)=E^\alpha_{\mathrm{SC}}(m,n)-\hat{E}(m,n) \quad , \tag{3}$$

we can now rewrite Eq. (1) relative to a reference configuration m^0,n^0 as

$$\begin{aligned}{}^{\Gamma}D_{\alpha\alpha}(m,n)-\hat{E}(m^0,n^0)={}&\Delta E^\alpha_{\mathrm{SC}}(m,n)\\ &+[\Delta(m,n;m^0n^0)+\Delta_{\mathrm{CF}}] \quad ,\end{aligned} \tag{4}$$

where $\Delta(m,n;m^0,n^0)$ is the difference between the average SC energy $\hat{E}(m,n)$ and that of the reference configuration $\hat{E}(m^0,n^0)$. Note that the single configuration *shift* $\Delta E^g_{\mathrm{SC}}(m,n)$ does not depend on A and that the A dependence reappears in $\hat{E}(m^0,n^0)$ (which is common to all terms and hence drops from the multiplet splitting), and in the second term in Eq. (4). This term, denoted Δ_{eff}, represents the average energy separation between the configurations (m,n) and (m^0,n^0), including both bare-ion ($\hat{H}_0$) and mean-field ($\langle \hat{H}_1 \rangle$) effects, and equals therefore the total energy difference

$$\Delta_{\mathrm{eff}}(m,n;m^0,n^0)=E_T(m,n)-E_T(m^0,n^0) \quad .$$

In the local density version of MF theory,[5-7] Δ_{eff} can be approximated well by the difference in transition state orbital energies. Evaluating $\hat{E}$ from Eq. (2), one obtains closed-form expressions for $\Delta E_{\mathrm{SC}}(m,n)$ of Eq. (3) as well as the off-diagonal elements, all in terms of B_0, C_0, λ_e, and λ_t alone. If theoretical MF values for λ_e, λ_t, and Δ_{eff} are available, the solution of the secular equation provides the multiplet corrections $\Delta E^{(i)}(m,n)$ to the total MF energy $E_T(m,n)$ for each multiplet $i={}^{2S+1}\Gamma$. Alternatively, one can isolate the extent of MC underlying the experimental data by fitting the absorption spectra,[1,2] obtaining experimental λ_e, λ_t, and Δ_{eff} values [Figs. 1(a)–1(c), where we have replaced for simplicity Δ_{eff} by a single configuration average value]. Using these parameters we calculate the multiplet correction $\Delta E^{(i)}$ for the ground state [Fig. 1(d)] as well as the correction $\Delta E^{(i)}-\Delta E^{(j)}$ for excitation between the multiplets i and j [Fig. 2(a)]. If we further assume that the orbital deformation parameters pertinent to excitations are approximately valid for ionization (different B_0 and C_0 values are available[8]), we can also estimate the MC to the ground state of the charged impurities A^+ and A^- [Fig. 2(b)] as well as their differences $\Delta H(-/0)$ and $\Delta E(0/+)$ which are the MC for the acceptor ($A^0 \rightarrow A^-$) and donor ($A^0 \rightarrow A^+$) transitions, respectively [Fig. 2(c)]. The key point is that our transformation identifies both bare-ion (Δ_{CF}) and average multiplet effects (Δ) in the crystal-field parameter Δ_{eff}, and that the configuration dependence in $A(m,n)$ is renormalized in Δ in a way that permits direct comparison with electronic structure calculations.[12]

Figures 1(a)–1(c) reveal chemically transparent trends in the mean-field parameters. The complicated S-shaped curve of Δ_{CF} obtained in the conventional models[2] and unmatched by state-of-the-art MF calculations[5-7] is replaced by a simple

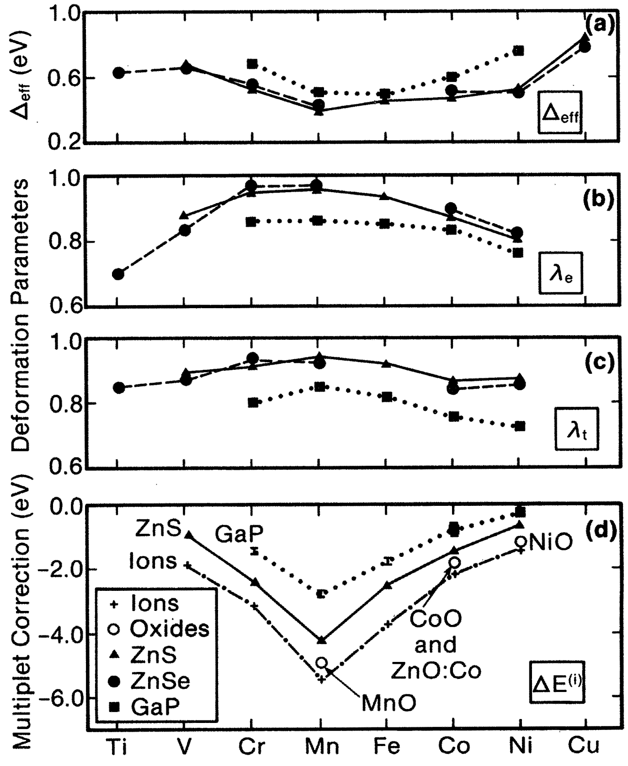

FIG. 1. Parameters for divalent $3d$ ion impurities: (a) effective crystal-field splitting; (b),(c), e and t deformation parameters; and (d) multiplet correction to the ground state.

one, showing a minimum at Mn and maximum for the heavier $3d$ impurities, as found in recent calculations,[5,6] an increase in Δ_{eff} with covalency (GaP vs II-VI compounds), and a decrease with lattice parameter. Our fits are as good, and usually better than those obtained previously in the standard approach[2,8,9] (e.g., in CoO, where the number of observed transitions exceeds the number of parameters, our method predicts the four unfitted transitions to within 0.02 eV). Previous discrepancies between calculations on bulk oxides and the conventional crystal-field fitted parameters are removed (e.g., in NiO, $\Delta_{\text{CF}}=1.13$ eV, and the calculated MF value[4] $\Delta_{\text{eff}}\cong 0.72$ eV. Our result is $\Delta_{\text{eff}}=0.75$ eV). The orbital deformation parameters [Figs. 1(b) and 1(c)] decrease rapidly with covalency, but are nevertheless substantially higher than those deduced from orbital integrated charges.[7] The MC to the ground-state energies [Fig. 1(d)] show a maximum for the high-spin impurity at the center of the $3d$ series (Mn^{2+}) and a rapid decrease with increasing covalency and decreasing spin at the two ends of the $3d$ series. Interestingly, we find a similar correction for the impurity system ZnO:Co and the pure bulk CoO [Fig. 1(d)], suggesting that most of the ground-state multiplet effects are induced by the nearest ligands. We find that the MC for bulk Mott insulators MnO, CoO, and NiO are intermediate between those of the free ions and the impurities in the sulfides [Fig. 1(d)]. Whereas MC to the ground-state total energy are relatively small [but sufficient to stabilize the high-spin ground state, cf. Figs. 1(d) and 2(b)], the corrections for excitations [Fig. 2(a)] and ionization [Fig. 2(c)] can be substantial on the physically relevant scale of the optical band gap. Surprisingly, one-electron theory is predicted to describe accurately the lowest excitation energies for all impurities but Mn, even in a relatively ionic host like ZnS [Fig. 2(a)]. In contrast, MC to the donor and acceptor energies are substantial for all impurities [Fig. 2(c)]. Adding these calculated corrections $\Delta H(-/0)$ and $\Delta E(0/+)$ to the observed single donor [heavy lines in Figs. 3(a) and 3(b)] and single-acceptor [heavy lines in Fig. 3(c)] energies in ZnS, ZnSe, and GaP, we obtain the position of the (transition state) e and t levels as should be obtained in MF elec-

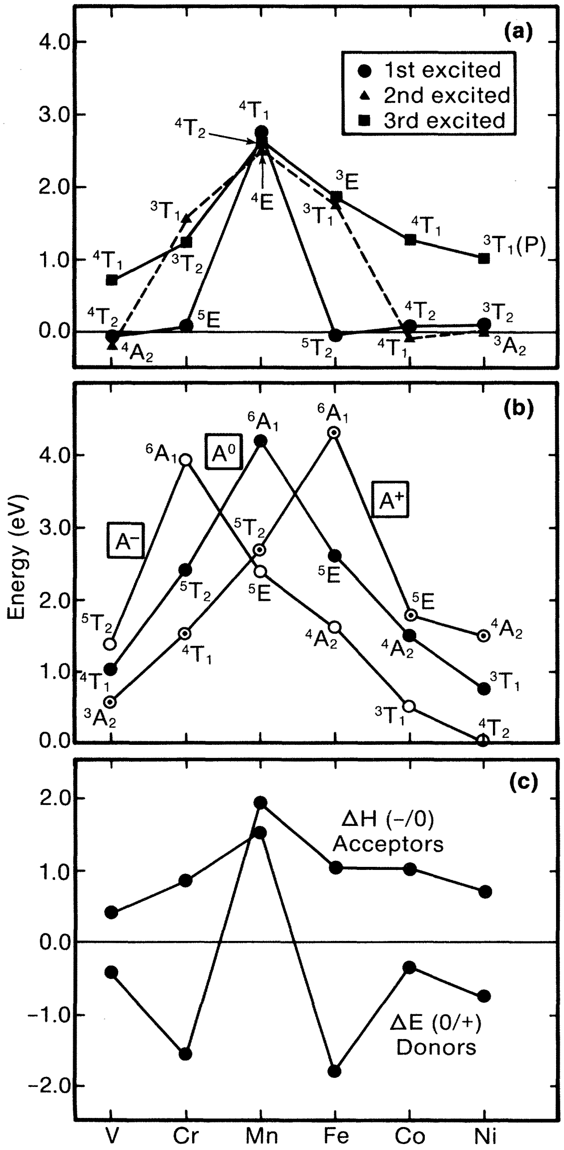

FIG. 2. Multiplet corrections in ZnS for: (a) excitations from the ground state of A^0; (b) the negative of correction for ground state of A^0, A^+, and A^-; and (c) acceptor and donor transitions.

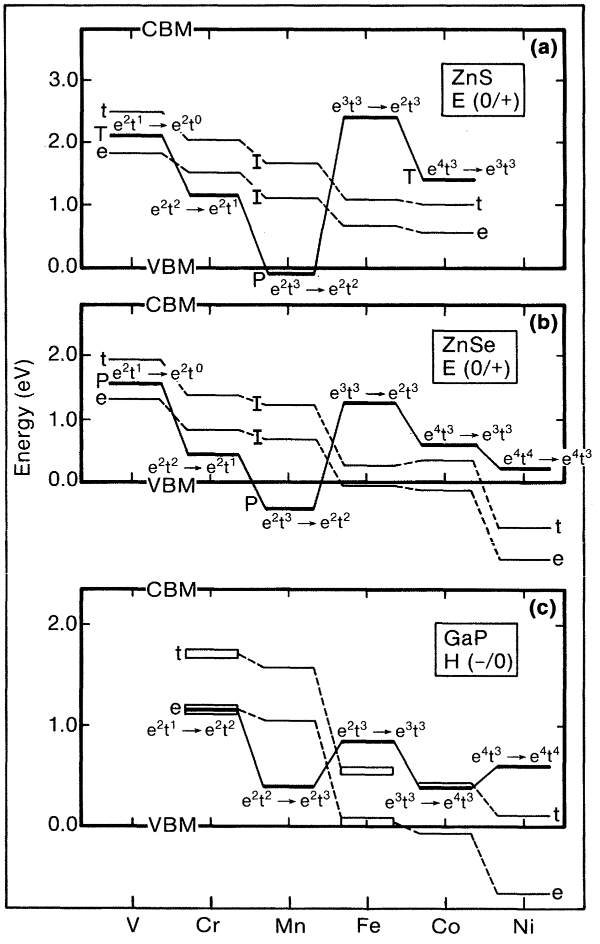

FIG. 3. Heavy lines: experimental donor energies in ZnS (a), ZnSe (b) and acceptor energies in GaP (c). Thin lines, the deduced duced MF (transition state) levels e and t (obtained from experimental energies by subtracting the multiplet corrections). T = tentative, I = interpolated, P = predicted.

tronic structure calculations (i.e., with no multiplet effects). We see that the large deformation parameters for Mn determined optically [Figs. 1(b) and 1(c)], combined with its high spin, produce the largest MC, pushing both the (controversial[1]) donor states in II-VI's semiconductors and the acceptor energies in III-V near the VB maximum and predict its disappearance in II-VI materials [Figs. 3(a) and 3(b)]. We find that the nonmonotonic trends in the MC for donor and acceptor transitions [Fig. 2(c)] are entirely responsible for the similarly nonmonotonic trends in the observed donor and acceptor activation energies both for covalent and ionic materials (Fig. 3). This explains the hitherto puzzling discrepancies between the monotonic trends in all calculated (transition state) e and t impurity levels[5–7] and experiment.[1] Finally, we note that this theory predicts that MC can produce a large correction ΔU to the Mott-Hubbard electronic repulsion parameter U [defined as the difference $E(0/+) - E(-/0)$]: using the results of Fig. 2(c), we find, for example, $\Delta U = -0.67$, -0.72, and -0.2 eV for Cr in ZnS, ZnSe, and GaP, respectively. The electronic repulsion energy U [0.55 eV in GaP (Ref. 6)] can hence be reduced both by screening (the self-regulating response[6]) and by many-electron effects. Combined with additional reduction by lattice relaxation, MC can produce "negative-U" systems.

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[12] Fitting the same data for ZnSe:Co by the approaches of Refs. 7 and 10 and the present one gives, respectively, λ_e values of 0.95, 0.945, and 0.894; λ_t values of 0.81, 0.81, and 0.844; and Δ_{eff} values of 0.90, 0.66, and 0.46 eV.