One-Electron Broken-Symmetry Approach to the Core-Hole Spectra of Semiconductors

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(Received 22 November 1982)

It is shown that in contrast to band theory, a self-consistent one-electron model with broken symmetries (crystal orbitals are not constrained to be Bloch periodic) provides a physical description of core-ionization, core-exciton, and core-to-conduction-band transition energies in semiconductors. Application to GaP shows that a hitherto unrecognized factor—the screening of the core-hole self-energy by the electron orbit—can explain many of the outstanding puzzles in core-hole spectra.

PACS numbers: 71.35.+z, 71.50.+t, 78.20.-e

With the recent advent of continuous-radiation light sources in the far uv, core spectroscopy has become a major characterization technique for studying the electronic structure of bulk[1-6] and surfaces[7] of semiconductors. Experimentally, the core-exciton binding energy δ has been defined[1-7] [c.f., Figs. 1(b) and 1(c)] as the difference $\delta = E_{\text{C, CBM}} - E_{\text{ex}}$ between the core (C)-to-vacuum ionization energy $E_{\text{C, CBM}}$ [referred to the relevant conduction-band minimum (CBM)] and the lowest optical excitation energy E_{ex} from a core level to a final electron orbit (exciton state). $E_{\text{C, CBM}}$ is determined by adding the value of the optical band gap E_g to the spin-orbit-corrected core-to-vacuum ionization energy $E_{\text{C,VBM}}$ [referred to the valence-band maximum (VBM)], as measured in photoemission.[8] The detailed data on a wide range of heteropolar semiconductors[1-7] present some intriguing puzzles. First, the measured values of δ for cations, e.g., GaP [0.238 ± 0.1 eV (Ref. 2, 4) or 0.6 eV (Ref. 1)], InP [>0.27 eV (Ref. 3)], PbSe [1 eV (Ref. 6)], is ~10 times larger than that of valence excitons or donor impurity levels which evolve from the same conduction-band extrema.[9] A broad range of shallow-donor tight-binding[10] and effective-mass-approximation (EMA)[11-13] calculations have likewise produced δ values that are 5–1000 too small [for GaP $\delta = 0.038$ (Ref. 2a)–0.05 (Ref. 10) eV, for PbSe $\delta = 0.001$ eV (Ref. 12)]. Second, despite the gross failure to explain δ, shallow-donor models have paradoxically predicted the spatial extent and the EMA character of the final electron state in the gap with remarkable accuracy.[3-5,12] Third, whereas one expected to find in the optical spectra below $E_{\text{C,CBM}}$ the exciton gap states, the observation of weakly perturbed and slightly downshifted (0.1–0.2 eV) CB extremum states there was convincingly demonstrated,[2-5] albeit described as a shocking discovery.[2b] Fourth, core spectroscopy showed[1,6] that the critical points in the CB final states observed a few electronvolts above $E_{\text{C, CBM}}$ were surprisingly downshifted by as much as 1.5 eV relative to the known positions of these states[1,6] both from VB → CB spectroscopy and from band theory. These large shifts are in sharp conflict with a weakly perturbed shallow-donor behavior.[9-13]

Previous theoretical models of core excitons in semiconductors[9-13] have identified the measured binding energy δ with the ionization energy δ_1 of the *gap* level relative to the CBM. The core-hole states, assumed to be unaffected by the occupation of the final electron states, were consequently eliminated from the models.[9-13] The theory of core excitons was mapped thereby into the theory of donor impurities. In this Letter I report the results of a first-principles self-con-

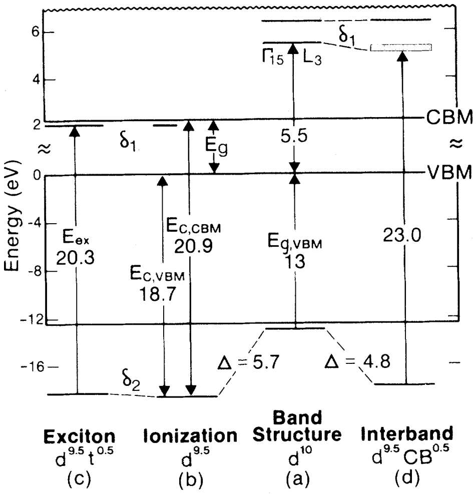

FIG. 1. Calculated self-energies for the (a) symmetry-constrained and (b)–(d) symmetry-broken solutions for core-hole excitations in GaP.

sistent calculation for core-hole excitations in GaP, treating directly screening, polarization, and relaxation effects for both the core hole and the electron gap states. It explains the paradoxical features of core-hole spectra in semiconductors by a hitherto unrecognized effect—the reduction δ_2 in the core-hole self-energy in excitation relative to ionization through additional relaxation-polarization by the electron orbit. Hence, $\delta = \delta_1 + \delta_2$, not[9-13] δ_1 ($\ll \delta_2$).

I describe the periodic ground state of the crystal by a self-consistent nonlocal pseudopotential[14] band structure with a filled Ga $3d^{10}s^2p^1$ configuration.[15,16] The one-electron energy taken from this band-structure model seriously underestimates the core-ionization energy: $E_{\mathrm{C,VBM}} = 13$ eV, compared with the experimental (spin-orbit averaged) result of 18.55 ± 0.10 eV.[8] Recognizing that the symmetry-constrained (band structure) version of one-electron theory prohibits by construction the formation of localized states with their attendant polarization and relaxation phenomena,[17] I now describe the final state in a broken-symmetry approach.[18,19] This is done by first performing a self-consistent pseudopotential band-structure calculation retaining only the sp^3 valence and conduction bands, and then replacing a single Ga atom by the $L = 0, 1, 2$ first-principles nonlocal pseudopotential[14] that sustains Ga $3d$ states on this site, *in addition* to the sp^3 bands. The electronic structure is then calculated self-consistently by use of the recently developed impurity Green's function method.[20] The ground state, associated with a self-consistent potential $V_G(\vec{r})$, is calculated by specification of a Ga $3d^{10}$ configuration and produces essentially the same spectrum (± 0.01 eV), Fig. 1(a), as the full band structure. The excited states, associated with self-consistent potentials $V_E(\vec{r})$, are calculated separately by use of the transition-state configurations $3d^{9.5}$ (core ionization) and $3d^{9.5}t^{0.5}$ (excitation into an electron orbit $|t\rangle$). The symmetry-breaking potentials of these "electronic impurities" are defined as $\Delta V(\vec{r}) = V_E(\vec{r}) - V_G(\vec{r})$. Note that in the broken-symmetry approach I do not constrain the charge density $\rho(\vec{r})$ to be periodic[1,6] or $\Delta V(\vec{r})$ to be weak[11] but otherwise use the same self-consistent (local density) theory used in band-structure calculations to describe the functional relationship $\Delta V[\rho]$. If the self-consistent $\Delta V(\vec{r})$ turns out to be weak and extended, the single-particle energies will approach the solutions ϵ_i of the symmetry-constrained (Bloch) problem. On the other hand, if the variational $\Delta V(\vec{r})$ becomes deep and short ranged, it can sustain also localized bound states with self-energies $e_i = \epsilon_i + \Delta_i$ that differ from the symmetry-constrained energies ϵ_i by the non-Koopmans term $\Delta_i = \Pi_i + \Sigma_i$, where Π_i and Σ_i denote the self-interaction cancellation energy and the relaxation energy, respectively.[17] Band theory[1,6] or coreless impurity models[9-11] assume both to vanish as $\Omega^{-1/3}$ since the eigenfunctions are extended over a large volume Ω. Furthermore, since Π_i and Σ_i are affected by *all* occupied states, the core self-energy in the ionization process $d^{10} \to d^9$ is now allowed to differ from the core self-energy in the excitation process $d^{10} \to d^9 t^1$, in contrast with band theory.

Core ionization: Figure 2 shows that the self-consistent symmetry-breaking potential ΔV for ionization is strong and localized about the excited atom, indicating that the success of band theory (with the assumption $\Delta V \to 0$) for VB → CB transitions[1,6] cannot be extended to C → CB transitions. Figure 1(b) shows that relative to band theory, the core-hole self-energy had moved down by $\Delta = 5.7$ eV, yielding a core-ionization energy $E_{\mathrm{C,VBM}} = 18.7$ eV, in good agreement with the experimental value 18.55 ± 0.1 eV.[8] I find $\Pi_d = 15.1$ eV and a relaxation energy $\Sigma_d = -9.4$ eV which is more negative by 2.7 eV than the free-atom relaxation energy. This reflects the extra atomic relaxation facilitated by the screening of the hole by the valence band.

Core exciton: The attractive $\Delta V(\vec{r})$ for ionization pulls down from the CB shallow unoccupied a_1, e, and t_2 donor levels [Fig. 1(b)]. In the calculation for the allowed p exciton [Fig. 1(c)] I occupy the lowest of these donor levels (t_2 symmetry, predominantly p type on Ga) by the emitted electron ($3d^{9.5}t^{0.5}$ configuration), and seek

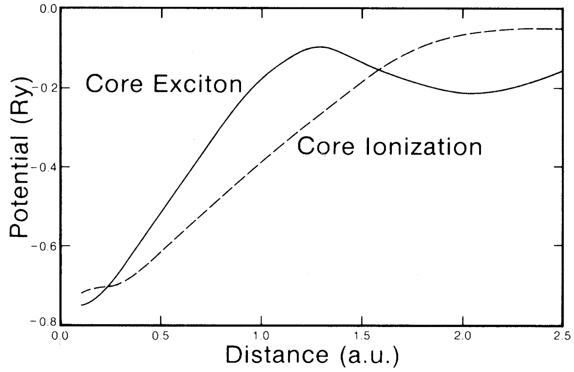

FIG. 2. The spherical part of the self-consistent symmetry-breaking potentials.

a new self-consistent $\Delta V(\vec{r})$ (Fig. 2). I find the antibonding Ga-like t_2 donor gap level at an energy $\delta_1 = 0.05 \pm 0.03$ eV below the CBM. In agreement with experiment[2-5] and with shallow-donor models[9-13] its electron orbit [Fig. 3(a)] is extended (only $q = 0.04e$ is enclosed within the near-neighbor sphere), sampling predominantly the secondary shallow minima in ΔV. Spectral analysis[20] reveals it to be composed predominantly from the host states in the lowest CB minima, which hence remain only weakly perturbed. δ_1 (an energy level) can hence be viewed as the response of the conduction bands to the attractive core-hole potential: Much like in shallow-donor models,[9-13] the weak long-range part of $\Delta V(\vec{r})$ pulls down a shallow level into the gap with a binding energy δ_1. However, a second, hitherto unrecognized contribution δ_2 to δ exists. Since $\Delta V(\vec{r})$ for excitation is less attractive than ΔV for ionization (Fig. 2) in the region where the hole orbital [Fig. 3(b)] is localized, *the hole self-energy moves up* by $\delta_2 = 0.35 \pm 0.15$ eV relative to its position for ionization. The total apparent binding energy $\delta = \delta_1 + \delta_2 = 0.40 \pm 0.15$ eV is "deep" in agreement with experiment.[1-5] Note that if one uses the correct one-electron threshold for *excitation* $E_{\mathrm{C,CBM}}{}^{E} = E_{\mathrm{C,CBM}} - \delta_2$, rather than the threshold $E_{\mathrm{C,CBM}}$ for *ionization* used previously,[1-6] it is no longer surprising to find[2] that the spectral features just above $E_{\mathrm{C,CBM}}{}^{E}$ are perturbed CB states, not exciton lines.

δ_2 (an energy-level shift) may be viewed as the occupation-dependent interaction of the electron orbit with all other states. It contains both the electrostatic potential of the electron orbit at the core, and the (incomplete) relaxation of the valence states (over and beyond the relaxation due to the core hole) by the penetration of the electron orbit. Shallow-donor models,[9-13] in equating δ with the ionization energy δ_1 of the gap level without allowing the remaining states to respond, have consistently underestimated the observed binding energy while still producing physically correct extended electron orbits. This is a reasonable approximation for *valence* holes or shallow impurities.[9] However, the self-energy e_d of a localized core hole decreases rapidly as the occupation N_t of an outer valence orbital increases. For example, total energy calculations (using the method of Ref. 17) for a free Ga ion (where $|t\rangle \equiv 4p$) show that it takes 13 eV more energy to ionize $d^{10} \rightarrow d^9$ than $d^{10}p^1 \rightarrow d^9p^1$, i.e., the d self-energy is $e_d(N_p) \cong \frac{1}{2} U_{pd} N_p$ with a large off-diagonal correlation energy $U_{pd} = 13$ eV. In heteropolar semiconductors where most of the VB charge resides on the anions, deep-cation core orbitals remain largely unscreened. Hence, even a weak localization q of an electron in the orbit $|t\rangle$ in the solid can release a nonnegligible relaxation energy $\delta_2 \approx \frac{1}{2} U_{td} q = 0.26$ eV. The δ_2 effect hence combines the excitation response of the core $\partial e_d / \partial N_t = U_{td}$ with the localization q of the electron orbit. In contrast to the dynamical correction,[13] it can be significant even if the electron is not tightly bound to the hole, but the hole has a large correlation energy. For core holes in metals or in chemisorbed atoms,[21] δ_2 (the relaxation shift) can be as large as 5–7 eV since the screening orbit is atomically localized ($q = 1$).

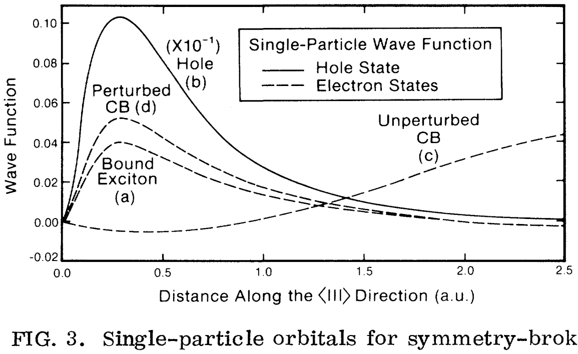

FIG. 3. Single-particle orbitals for symmetry-broken solutions.

Core interband transitions: If we assume that the residence time of an excited electron in a bound CB resonance is sufficiently longer than its scattering time, we can calculate also $\delta_2(E)$ for C $\rightarrow$ CB transitions [Fig. 1(d)]. The shifts in the position of final CB states depend sensitively on their amplitude $q(E)$ on the cation site. Free-electron-like CB orbitals [Fig. 3(c)] appearing at 6.4 eV above the VBM are found to be almost unshifted relative to the band-structure prediction [Figs. 1(a) and 1(d)]. On the other hand, CB states near Γ_{15c} and L_{3c} at $\approx E_{\mathrm{VBM}} + 5.5$ eV, having significant amplitudes on the cation [Fig. 3(d)], are shifted down by as much as 1.2 [$\delta_1 = 0.3$ eV, $\delta_2 = 0.9$ eV Fig. 1(d)], being now at $E_{\mathrm{VBM}} + 4.3$ eV (23 eV above the core level). This can explain the hitherto mysterious $E_{\mathrm{VBM}} + 4.15$ eV ($h\nu = 22.3$–22.8 eV) structure observed in core spectroscopy[2c] with no counterpart in VB $\rightarrow$ CB spectroscopy. I conclude that core spectroscopy does not measure the unperturbed CB structure as initially expected, but rather excitonic resonances [shaded in Fig. 1(d)] modulated by the variations $\delta_2(E)$ in the core-hole self-energy.

The model provides simple rules for estimating chemical trends in δ from information about $q(E)$. It explains why surface-cation core excitons have a larger binding energy than in the bulk[7] in terms of the strong cation character of the dangling-bond electron states. In contrast, this theory predicts that anion core excitons will be shallower ($\delta \approx \delta_1$) when the final orbital has little amplitude on the anion (e.g., the Γ_{1c} state). This is consistent with the absence of Sb (4*d*) core excitons in GaSb (Ref. 7a) and As (3*d*) excitons in GaAs,[7b] in contrast to the rather deep cation core excitons in these systems. Likewise, the large excitonic shift of the X_c point in InP relative to GaP (Ref. 3) can be naturally explained by the larger cation content of the wave function in the former case.

I gratefully acknowledge useful discussions with D. Aspnes, M. L. Cohen, R. Enderlein, W. Harrison, and S. Kelso.

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[1] P. Thiry, Y. Petroff, R. Pinchaux, J. R. Chelikowsky, and M. L. Cohen, Solid State Commun. 20, 1107 (1976).

[2a] D. E. Aspnes, C. G. Olson, and D. W. Lynch, in *Proceedings of the Thirteenth International Conference on the Physics of Semiconductors, Rome, 1976* (North-Holland, Amsterdam, 1977), p. 1000.

[2b] D. E. Aspnes, in *Festkörperprobleme XVII*, edited by J. Trensch (Vieweg, Braunschweig, 1977), p. 235.

[2c] D. E. Aspnes, C. G. Olson, and D. W. Lynch, Phys. Rev. B 12, 2527 (1975).

[3] S. M. Kelso, D. E. Aspnes, C. G. Olson, D. W. Lynch, R. E. Nahory, and M. A. Pollack, Jpn. J. Appl. Phys. 19, 327 (1980).

[4] D. E. Aspnes, S. M. Kelso, C. G. Olson, and D. W. Lynch, Phys. Rev. Lett. 48, 1863 (1982), and private communication.

[5] S. M. Kelso, D. E. Aspnes, C. G. Olson, D. W. Lynch, and D. Finn, Phys. Rev. Lett. 45, 1032 (1980).

[6] G. Martinez, M. Schlüter, and M. L. Cohen, Phys. Rev. B 11, 660 (1975).

[7a] D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 1624 (1975).

[7b] R. S. Bauer, J. Vac. Sci. Technol. 14, 899 (1977).

[8] L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B 9, 600 (1974).

[9] See recent reviews: M. Altarelli, J. Phys. (Paris), Colloq. 34, C4-95 (1973); F. Bassani, Appl. Opt. 19, 4093 (1980).

[10] H. P. Hjalmarson, H. Büttner, and J. D. Dow, Phys. Rev. B 24, 6010 (1981).

[11] S. T. Pantelides, Solid State Commun. 16, 217 (1975); M. Altarelli, Phys. Rev. Lett. 46, 205 (1981).

[12] F. Bechstedt, R. Enderlein, and M. Koch, Phys. Status Solidi 99(b), 61 (1980).

[13] A. Quattropani, F. Bassani, G. Margaritondo, and G. Tinivella, Nuovo Cimento B 51, 335 (1979); G. Strinati, Phys. Rev. Lett. 49, 1519 (1982).

[14] A. Zunger, Phys. Rev. B 22, 649 (1980).

[15] The local-density formalism overestimates the 3*d* ionization energy of a Ga atom {total energy differences $\Delta E = 26.9$, 30.5, and 36.2 eV for exchange coefficients $\alpha = \frac{2}{3}$, 0.8, and 1, respectively, relative to experiment [W. Lotz, J. Opt. Soc. Am. 60, 206 (1970)] $\Delta E = 21 \pm 3$ eV}. I apply an empirical adjustment to fit the data for the free atom by adding a positive square well to the $L = 2$ Ga ionic pseudopotential at small r and use $\alpha = 1$. This pseudopotential is used with no further adjustment in all solid-state calculations.

[16] Lotz, Ref. 15.

[17] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[18] A. Zunger and A. J. Freeman, Phys. Rev. B 16, 2901 (1977).

[19] H. Agren, P. S. Bagus, and B. O. Roos, Chem. Phys. Lett. 82, 505 (1981).

[20] U. Lindefelt and A. Zunger, Phys. Rev. B 26, 896 (1982), and 27, 1191 (1983).

[21] A. R. Williams and N. D. Lang, Phys. Rev. Lett. 40, 954 (1978), and Phys. Rev. B 16, 2408 (1977).