Indirect interaction between localized impurities in polar semiconductors

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The electronically mediated indirect interaction between localized impurities, each of which generates an isotropic local disturbance on the substituted metallic ion sites, in polar semiconductors with different band-edge-state parities is studied. The second-order-perturbation energy is evaluated with an interband matrix element, which is consistent with the hybridization of the basic states involved in the interband transitions. The calculated indirect interaction exhibits a characteristic change from negative to positive as the separation distance increases and decays exponentially in the long-range region.

For a local disturbance in a solid arising from, for example, a neutral point defect or an impurity with a localized magnetic moment, its direct influence is limited to the immediate vicinity of the disturbance site. But there exists an electronically mediated indirect interaction, which may have a longer range. The indirect interaction may be mediated by the polarization of the valence-band electrons due to their direct interaction with the separated localized impurities. The polarized Bloch electrons will then mediate an indirect interaction between two separated local impurities. The polarization process in a semiconductor involves interband electron-hole excitations that depend on the band structure of the host semiconductor. This indirect interaction is similar to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction¹ in metallic magnetic alloys or the Bloembergen-Rowland indirect-exchange mechanism² in insulators. The indirect interaction induced by the odd-parity-potential perturbation arising from the atomic displacement associated with phonon excitations was discovered by Sokel and Harrison³ to explain the flattening of the transverse-acoustic-phonon dispersion relation. A similar form of the interband transition matrix element, i.e., a constant, was also adopted by Liu⁴ to study the exchange-polarization effects in narrow-gap semiconductors. In this paper, confined to the isotropic perturbing potential, the indirect interaction is studied with an interband transition matrix element which is consistent with the symmetry of the basic states involved in the electron-hole excitation and the hybridization of basic states in the energy band.

Assuming a perturbing potential V due to the point disturbance, we can obtain the electron mediated interaction between two impurities separated by a distance $\mathbf{R}$, using second-order-perturbation theory:

$$H(\mathbf{R}) = -\frac{1}{\Omega^2} \sum_{nn', \mathbf{k}\mathbf{k}'} \left[\frac{|V_{nn'}(\mathbf{k}, \mathbf{k}')|^2 e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}}}{E_{n'}(\mathbf{k}') - E_n(\mathbf{k})} + \text{c.c.} \right], \quad (1)$$

where $E_{n'}(\mathbf{k}')$ and $E_n(\mathbf{k})$ are the conduction band (with band index n') and valence-band energy, respectively.

Here Ω is the volume of the crystal, and the wave vectors $\mathbf{k}'$ and $\mathbf{k}$ are to be summed over the first Brillouin zone (BZ). The interband matrix element $V_{nn'}$ is evaluated with the impurity site as the origin, and the change of phase of the Bloch function over the two impurity sites gives rise to the phase factor $e^{i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}}$.

Consider now a direct-gap semiconductor with s - and p -band edges located at the Γ point. At this point, the interband matrix element of an isotropic perturbation between an s -like and a p -like state does not exist. Away from the Γ point, s - p mixing in the band state occurs. Only then interband excitations become possible. The s - p mixing of band states depends on the symmetry of the basic states used to represent the band states and the lattice structure. For polar semiconductors with zincblende structure, the matrix element of the unperturbed crystal Hamiltonian between s and p states varies with $\mathbf{k}$ as (Slater and Koster⁵)

$$(s/z) = \frac{8i}{\sqrt{3}} I_{sp\sigma} \sin \frac{ka}{4}, \quad (2)$$

for $\mathbf{k}$ along the $[001]$ direction. Here $I_{sp\sigma}$ is the two-center energy integral of s and p orbitals, and a denotes the lattice constant. The crystal Hamiltonian matrix element (s/z) in Eq. (2) shows that, while there is no s - p mixing between band states at the Γ point, the s - p mixing gets to maximum at the X point, i.e., $(0, 0, 2\pi/a)$. For the case that the isotropic local disturbance is generated by a substitutional impurity on a metallic ion site, the perturbing potential V will couple strongly only with the s -like state because both are centered on the same point and with the same parity. Since the s - p mixing is closely related to the matrix element (s/z) , we assume that the interband matrix element $|V_{nn'}(\mathbf{k}, \mathbf{k}')|^2$ is isotropic as

$$|V_{nn'}(\mathbf{k}, \mathbf{k}')|^2 = |J|^2 \sin^2 \left[\frac{ka}{4} \right], \quad (3)$$

where k is the wave vector of the valence band, and J is the matrix element of V between s -like basic states. This assumption neglects the reduction of the s -state component accompanied with the mixing of the p state in the conduction band near the zone boundary region. We

note that the interband transition of p -like states is neglected in Eq. (3), and this is justified only if the matrix element of V between p -like states is negligible. If the isotropic potential perturbation arises from the substitution of an impurity on the metallic ion site, the dominant transitions are those between s -like states only. In this case the assumed form of the matrix element in Eq. (3) will be more justifiable. We assume that the energy band structure of the semiconductor with direct energy gap E_g at the Γ point is

$$E_c(\mathbf{k}') = E_g + \frac{\hbar^2 k'^2}{2m_e}$$

and

$$E_v(\mathbf{k}) = -\frac{\hbar^2 k^2}{2m_h}, \quad (4)$$

where m_e and m_h are the electron and hole effective mass, respectively.

The double summations in Eq. (1) can be transformed into double integrations over the BZ. In evaluating the integral, we extend the integration limit for k and k' to infinity. The spurious contribution arising from this is quite negligible. The final result of the interaction energy is

$$H(R) = -\frac{|J|^2 m_e E_g \sqrt{m_e m_h}}{2\pi^3 \hbar^4 R} \left[\frac{1}{R(\alpha^2 + 1)} K_2(k_h R \sqrt{\alpha^2 + 1}) - \frac{1}{2} \left[\frac{R + a/2}{R^2 + \alpha^2(R + a/2)^2} K_2(k_h \sqrt{\alpha^2(R + a/2)^2 + R^2}) + \frac{R - a/2}{R^2 + \alpha^2(R - a/2)^2} K_2(k_h \sqrt{\alpha^2(R - a/2)^2 + R^2}) \right] \right], \quad (5)$$

for $R > a/2$, and

$$k_h^2 = 2m_h E_g / \hbar^2, \quad \alpha^2 = m_e / m_h. \quad (6)$$

The function K_2 in Eq. (5) is the modified Bessel function of second order. Using the asymptotic expansion formulas for the function K_2 in two limiting cases, we obtain, in the case of $k_h R \gg 1$,

$$H(R) \simeq \frac{|J|^2 \mu E_g}{2\pi^3 \hbar^4 R^2} \left[\frac{\pi m_e m_h}{2k_g R} \right]^{1/2} \left\{ \cosh \left[a \left(\frac{2m_e^2 E_g}{(m_e + m_h) \hbar^2} \right)^{1/2} \right] - 1 \right\} e^{-k_g R}, \quad (7)$$

where

$$\mu = \frac{m_e m_h}{m_e + m_h}, \quad k_g^2 = 2(m_e + m_h) E_g / \hbar^2. \quad (8)$$

On the other hand, if $k_h R \ll 1$, we obtain

$$H(R) \simeq -\frac{\mu^2 |J|^2}{2\pi^3 \hbar^2 \sqrt{m_e m_h} R^4}. \quad (9)$$

The result of Eq. (5) shows that while the interaction energy between two separated impurities is negative at small intersite distance, it turns out to be positive and exponentially decaying in longer range. The turning point is at about 10 lattice constants. If an additional Lorentzian-like form factor, e.g., $(k'^2 + \beta^2)^{-2}$ with constant β , is included in Eq. (3) to reduce the overestimated contribution arising from the $\mathbf{k}'$ integration of the conduction band around the zone boundary region and beyond, the turning point will be reduced to about 0.7 lattice constant or the nearest-neighboring intersite distance in a fcc lattice. This result indicates an attractive indirect interaction in a near-neighboring pair, while beyond the turning point, the interaction will become

repulsive. This may suggest a mechanism for the formation of a cluster of impurities in polar semiconductors. In case of dilute magnetic impurity in semiconductors, such as the magnetic Mn^{2+} ions in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ or $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, the corresponding conclusion is that at small intersite distance, the indirect exchange interaction between two magnetic impurities may be ferromagnetic, while beyond that, it becomes antiferromagnetic. We note that, in spite of the different model approach, the properties of the indirect interaction given by Eq. (5) are qualitatively similar to that of our previous work.⁶ By comparison, the Sokel-Harrison mechanism³ with odd parity perturbing potential always mediates an attractive indirect interaction within the full range. Since the doping of magnetic impurities into the semiconductor will generate both the local crystal potential disturbances and the localized magnetic moments, the foregoing argument may provide a mechanism to explain both the formation of magnetic ion clusters and the characteristic change of the indirect exchange interaction with the interspin distance in some dilute magnetic semiconductors.^{7,8}

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