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Dependence of transition-metal impurity levels on host composition in III-V semiconductors

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Model calculations of substitutional transition-metal impurities in III-V semiconductors have been performed with the purpose of investigating how the defect energy levels vary as the host composition is changed. The calculations are based on the theory of Haldane and Anderson and include electron-electron interactions in a self-consistent manner. The band structure has been described in terms of an sp^3 second-nearest-neighbor tight-binding approximation. We find that the transition-metal acceptor energy levels have fixed positions relative to the average vacancy level or the vacuum level independent of the chemical composition of the host material. This stability is a consequence of self-consistent competition between the strongly localized Coulomb interaction at the impurity site and the hybridization with the nearest neighbors.

I. INTRODUCTION

In recent years there has been much theoretical and experimental activity focused on the study of the electronic structure of deep centers in semiconductors. A particularly important and interesting problem of this class of defects is the structure of the transition-metal impurities. Although a considerable amount of experimental data on these defects has accumulated[1,2] the microscopic understanding of all the factors affecting the transition-metal energy levels is not complete. Any attempt to treat the problem of the energy levels introduced by the transition-metal atoms has to address an important dichotomy. When a transition-metal ion is placed in a semiconductor some of its free-ion properties are preserved. On the other hand, the many charge states that are found in the band gap and the reductions in the g factors and spin-orbit couplings point to a strong interaction with the host states.[1] Therefore, in considering the problem of transition-metal impurities, one has to include both short-range interactions as well as overlap effects with the wave functions of the host material. Because of this, the most commonly used theoretical techniques, such as effective-mass theory or crystal-field theory are not applicable to transition-metal impurities.

Recently the problem of precisely predicting or measuring the energy levels of the transition-metal impurities in semiconductors has become especially important because these levels have been found to provide relatively accurate energy references from which to measure changes in the band structure of the host material.[2] Based on this finding a method for determining the band offsets or semiconductor heterointerfaces has been proposed.[3,4] An extension of this method has been employed to measure band-edge deformation potentials in GaAs and InP.[5] In theoretical attempts to explain the experimentally observed alignment of transition-metal energy levels between different materials, a critical role is played by the choice of the energy reference level. In the two-level model of Caldas *et al.*[6] or in the three-level model proposed later by Zunger,[7] the vacuum energy is considered to be the reference level. In the defect molecule model used by Tersoff and Harrison,[8] the cation vacancy and later by Langer *et al.*,[9] the average vacancy energy play the role of the energy references from which to measure band offsets.

In this paper we present theoretical calculations of the transition-metal energy levels in III-V semiconductors. The calculations are based on a model proposed by Haldane and Anderson.[10] The main purpose of this study is to use a model which can accurately predict trends in the transition-metal energy levels as the host material is changed, but which is still simple enough to provide direct physical insight into the most important factors controlling the location of the transition-metal energy levels. We have employed the Haldane-Anderson approach because it allows for a self-consistent treatment of the problem and also explicitly depends on the density of states of the host material. The trends in the changes in energy of the transition-metal impurity levels as the host material is altered should be well represented by this model.

II. FORMULATION OF THE TRANSITION-METAL PROBLEM

A. General

The theoretical analysis used here is a modified version of the Haldane and Anderson model with the semiconductor band structure described in terms of a tight-binding approximation. We assume the impurity concentration is sufficiently low to guarantee that the interactions between impurities are negligibly small. Within this assumption the Hamiltonian for a single transition-metal impurity atom in a semiconductor is given by

$$H=E_d \sum_{m,\sigma} n_{m\sigma}+\tfrac{1}{2}U \sum_{\substack{m,\sigma,m',\sigma' \\ [(m,\sigma)\neq(m',\sigma')]}} n_{m\sigma}n_{m'\sigma'}+\sum_{k,\sigma} \varepsilon_k n_{k\sigma} + \sum_{k,m,\sigma} (V_{mk}c^{\dagger}_{m\sigma}c_{k\sigma}+V_{km}c^{\dagger}_{k\sigma}c_{m\sigma}) \tag{1}$$

where ε_k and $n_{k\sigma}$, are, respectively, the energies and occupancies of the extended semiconductor states, E_d and $n_{m\sigma}$ are the energies and occupancies for the localized states on the impurity, U is the intra-atomic Coulomb interaction between d electrons, and V_{km} is the covalent admixture matrix element between localized and band states.

In a lattice of cubic symmetry d orbitals split under the influence of the crystal field into two levels, the two-fold degenerate e and the threefold degenerate t_2 state. In the following, we neglect this splitting. Solving Eq. (1) in the Hartree-Fock approximation and using the Green's-function method we obtain

$$E_{\text{def}}=E_d+9Un , \tag{2}$$

where

$$n=\sum_{\sigma} \tfrac{1}{10}(2n_{e\sigma}+3n_{t_2\sigma}) \tag{3}$$

and $n_{\alpha\sigma}$ $(\alpha=e,t_2)$ have the form

$$n_{\alpha\sigma}=Z^1_{\alpha\sigma}(E_{\text{def}})+Z^2_{\alpha\sigma}(E_{\text{def}}) \tag{4}$$

and

$$Z_{\alpha\sigma}(E_{\text{def}})=\frac{1}{\pi}\int_{-\infty}^{\varepsilon_v} G_{\alpha\sigma}(E)dE , \tag{5}$$

$$Z^2_{\alpha\sigma}(E_{\text{def}})=\left[1-\frac{d}{dE}\text{Re}\Sigma_\alpha(E)\right]^{-1}_{E=E_\alpha} N_{\alpha\sigma}(E_\alpha) , \tag{6}$$

$$G_{\alpha\sigma}(E)=[E-E_{\text{def}}-\Sigma_\alpha(E)]^{-1} , \tag{7}$$

$$\Sigma_\alpha(E)=\sum_{k,n}\frac{|V_{\mathbf{k}\alpha}|^2}{E-E_{n\mathbf{k}}} , \tag{8}$$

where $N_{\alpha\sigma}$ is the occupation number of the gap level appearing at the energy E_α, which is given by a solution of the equation

$$E_\alpha-E_{\text{def}}-\text{Re}\Sigma_\alpha(E_\alpha)=0 . \tag{9}$$

The impurity atom is characterized by the parameters E_d and U and the semiconductor states by the band structure E_{nk}. The interaction between d and k states is represented by the matrix element $V_{\mathbf{k}\alpha}$. We have neglected exchange energies which are essential to determine the actual energies of the transition-metal impurities. However, they are not important in our case because we are only concerned with the energy difference between the levels of the same transition metal in different semiconductors. The Coulomb interaction between the host electrons and between the host and impurity electrons has also been neglected in Eq. (1), but this interaction can be partly accounted for by making a suitable choice of U. We also do not include long-range interactions which have appreciable effects only for shallow levels.

In order to solve Eqs. (2) and (9) self-consistently for different occupancies of the defect, we have to evaluate the self-energy term Σ_α.

B. Evaluation of Σ_α

The calculation of the self-energy can be simplified by using the symmetry of the Brillouin zone and by using the crystal point group to reduce the number of independent elements. From Eq. (8) we have

$$\Sigma_\alpha=\frac{1}{N}\frac{V}{(2\pi)^3}\sum_{\gamma,\beta}\sum_{i,j}\sum_{n}\int d^3k\frac{S^{ijn}_{\gamma\beta}(k)}{E-E_n(k)+i\varepsilon} \times E_{\alpha\gamma}(p,q,z)E_{\gamma\beta}(s,t,v) , \tag{10}$$

where

$$S^{ijn}_{\gamma\beta}(k) =\sum_{s=1}^{48} A^{n*}_j(R_s\mathbf{k})A^{n}_{\beta}(R_s\mathbf{k})\exp[iR_s\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_i)] . \tag{11}$$

The integral over $\mathbf{k}$ in Eq. (10) is taken over $\frac{1}{48}$ of the Brillouin zone. R_s are symmetry operators of the cubic lattice. Because of the symmetry of the first Brillouin zone $E(R_ik)=E(k)$. $A^n_j(\mathbf{k})$ are eigenvectors and are obtained together with $E_n(k)$ by diagonalization of the host Hamiltonian. The host Hamiltonian is taken to be the empirical sp^3 second-nearest-neighbor tight-binding model Hamiltonian of Das Sarma and Madhukar.[11] $E_{\alpha\gamma}(p,q,z)$ and $E_{\gamma\beta}(s,t,v)$ are Slater-Koster integrals and p,q,z and s,t,v are directional cosines of $\mathbf{r}_j$ and $\mathbf{r}_i$, respectively. The sum i,j extends over the first nearest-neighbors of the impurity atoms. The index α corresponds to the t_2 of e character of the d orbital. Subscripts γ,β refer to the s, p_x, p_y, p_z character of the host atomic orbitals. $\underline{S}$ is a 16×16 matrix symmetric in both γ,β and i,j:

$$\underline{S}=\begin{bmatrix} \underline{S}_1 & \underline{S}_2 & \underline{S}_3 & \underline{S}_4 \\ \underline{S}_2 & \underline{S}_1 & \underline{S}_5 & \underline{S}_6 \\ \underline{S}_3 & \underline{S}_5 & \underline{S}_1 & \underline{S}_7 \\ \underline{S}_4 & \underline{S}_6 & \underline{S}_7 & \underline{S}_1 \end{bmatrix} .$$

The independent 4×4 matrices $\underline{S}_1$ to $\underline{S}_7$ are given in the

Appendix. The integral over the first Brillouin zone has been performed by the modified Lehman-Taut method[12] by dividing the first Brillouin zone into 256 tetrahedra.

III. NUMERICAL RESULTS AND DISCUSSION

In order to apply the preceding theory to the problem of transition-metal impurities in different III-V semiconductors one has to calculate $E_{n\mathbf{k}}$, V_d, E_d, and U. The band structure represented by the parameter $E_{n\mathbf{k}}$ is described using the tight-binding approach in the form given in Ref. 11. The covalent admixture matrix element $V_{\mathbf{k}\alpha}$ between d states and $\mathbf{k}$ states have been taken as Slater-Koster two-center nearest-neighbor integrals. This approximation is reasonable because we know that the probability of finding a $3d$ electron within the sphere of radius $r=1.5$ a.u. lies between 0.7 to 0.9 for Ti to Ni.[13] The radius $r=1.5$ a.u. is approximately 30% of the nearest-neighbor distance in III-V semiconductors. Therefore we can neglect overlap from the next-nearest neighbors. The numerical values of the Slater-Koster integrals have been obtained using the Harrison prescription for determining the s-d and p-d matrix elements.[14]

We have found that although the numerical values of parameters describing the properties of a specific transition-metal atom are crucial for characterizing differences between different transition-metal impurities in the given host, these parameters are not important when one considers how the transition-metal energy changes as the host band structure is changed through altering the thermal composition of the compound semiconductor. The parameters E_d have been estimated using Herman-Skillman calculations assuming that the free-atom energy level is given by

$$E_{d_0}=E_d+U_d(n-1)\ , \tag{12}$$

where U_d is the effective Coulomb interaction[15] and n is the number of d electrons occupying the d shell. In solids, the short-range Coulomb intra-atomic parameter is reduced by two effects: (1) hybridization of the d-electron wave function with the sp^3 hybrids, and (2) screening of the long-range interactions. These effects combined give an effective Coulomb interaction. The Coulomb interaction parameter U is difficult to derive from first principles. We have approximated it as the difference between the first and second ionization potentials of the free ion multiplied by a reduction factor (equal to 0.72) commonly used in crystal-field theory.[16] The parameters E_d and U are closely related. A change of E_d must be accompanied by a change of U of the same order of magnitude. We have found that the results are relatively insensitive to the choice of E_d. A change in E_d by 1 eV changes the energy of the transition metal in the gap by roughly 0.1 eV. The parameters characterizing the transition metals are given in Table I.

TABLE I. Transition-metal parameters (eV).

	Ti	V	Cr	Mn	Fe	Co	Ni
E_d	−13.5	−18.0	−25.0	−31.0	−38.0	−48.0	−60.0
U	6.8	7.5	8.0	8.2	8.3	9.2	10.5

The energy levels of the acceptor state (0/−) have been calculated assuming that the introduction of the transition-metal impurities does not affect the energy band structure of the host material. The results of the present calculations are given in Figs. 1–3. In Fig. 1 the position of the acceptor energy levels for several transition metals in GaP, GaAs, and InP are shown. The common energy reference is the GaP valence band edge located at ~6 eV below vacuum energy. It is seen in this figure that the locations of the transition-metal acceptor energies are approximately the same (within 0.2 eV) for the different host materials. In Fig. 2, the results for the identical calculation but with the parameters E_d and U reduced by 25%, are presented. Although the positions of the transition-metal impurity levels have changed with respect to the GaP valence band edge, the change is the same for each semiconductor. Therefore we conclude that the relative stability of transition-metal defect levels is not sensitive to the exact details of the parameters chosen for the calculation.

As seen in Fig. 3 the transition-metal energy levels also exhibit good stability when referenced to the average vacancy energy in each of the materials. This is not surprising because the position of the average vacancy energy (which is equivalent to Tersoff's neutrality point[17] or Cardona's midgap energy[18]) is determined by the density of states of the host semiconductor. In turn, the density of states of semiconductors within a class of isovalent semiconductors are strikingly similar if one considers the energies at which the maximum density of states occur and neglects the small density of states that arise from the details of the band structure. From these considerations, we conclude that the positions of the transition-metal energy levels in the band gap depend on the short-range impurity potential, which leads to different level structure for different elements. Yet the change of the

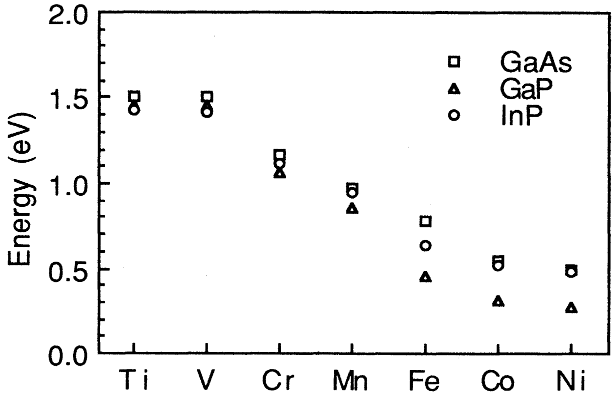

FIG. 1. Positions of the transition-metal acceptor levels in GaAs, InP, and GaP. The energy of the valence-band maximum of GaP is taken as zero for illustration.

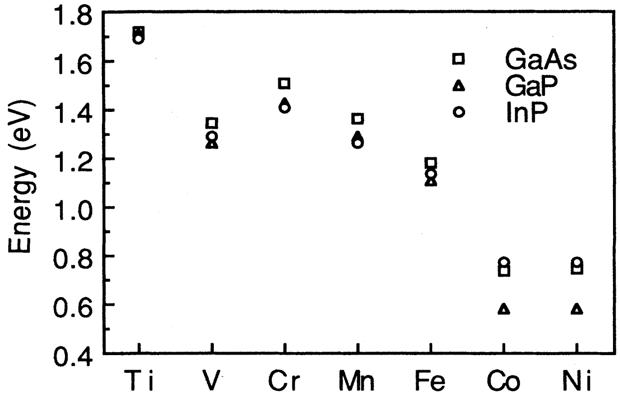

FIG. 2. Positions of the transition metals as in Fig. 1, but with the parameters E_d and U reduced by 25%. The Ni level is more sensitive to changes in the parameters than the Ti level is.

defect energy levels with changes in the semiconductor host are determined by hydridization, which we have found to be much the same for all group-III-V semiconductors. The most important contribution to the self-energy of the t_2 defect levels comes from the t_2-like states of the host crystals. These crystals states have a maximum density of states that are the origin of the optical (or Jone's zone) gap of the semiconductor. The width of the optical gap is again similar for all the III-V materials which further helps explain the stability of the transition-metal levels as the chemical composition of the host is altered. Those conclusions are in full agreement with a recent analysis of experimental data on band offsets.[19] It has been shown that, within the currently available accuracy of experiment, the energy difference between vacuum level and neutrality point (or average vacancy energy) is the same for all III-V semiconductors.[19,20] Therefore both energies provide the proper energy reference for a determination of the band offsets at semiconductor interfaces.

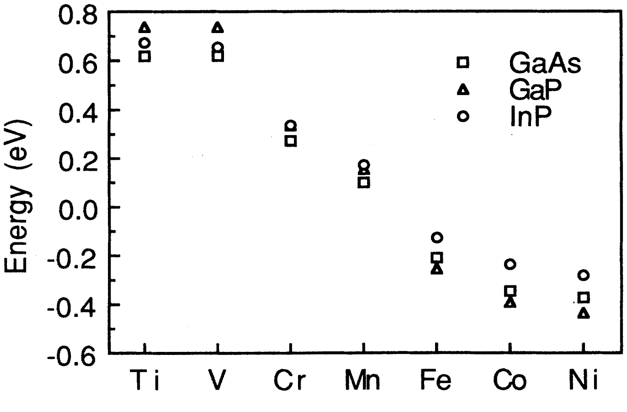

FIG. 3. Positions of the transition-metal levels with respect to the average vacancy energy for each material. The Ti and V energy levels have excellent stability as the semiconductor is changed. The Co and Ni levels, however, show a dependence on the host material.

An additional result of our calculations concerns the stability of the different transition metals. In particular, we find that the lighter transition metals, such as Ti or V, are not sensitive to changes in the host, but that the energies of the heavier metals, such as Co or Ni, depend to a greater degree on the specific band structure of the host semiconductor. The lighter transition-metal levels should therefore be expected to have a greater stability as the host chemical content is altered and should be more accurate in predicting band offsets or deformation potentials.[21] The relatively higher stability of Ti and V compared to Co and Ni has a straightforward explanation. The heavier atoms do not hybridize as strongly with the host sp^3 levels as do the lighter elements. Therefore the defect levels associated with the heavier atoms are more sensitive to E_d and to U, and lose the stability that is imparted to the defect structure by the similarities of the III-V semiconductor band structures. We must emphasize that the self-consistency of our model is an integral feature which must be included to quantity the degree of stability of the transition-metal energy levels.

IV. CONCLUSIONS

In this paper, we have addressed the problem of defining the origin of the stability of transition-metal energy levels as the host material is altered. The calculations were based on a model that is capable of providing accurate results, yet retains the essential physics to allow an identification of the processes that cause the stability. The stability is a consequence of the close similarity of the gross features of the band structures within a class of isovalent semiconductors, in this case the III-V semiconductors. It is found that the values for U are finite and allow for a significant charge transfer between the d electrons and the host sp^3 hybrids that is a function of the transition metal chemical species. The parameter U therefore plays an important role in determining the energy positions of the impurity levels within a given semiconductor. On the other hand, the charge transfer that occurs between the transition metal and the host sp^3 hybrids for a given transition metal remains relatively insensitive to the host material, and therefore does not contribute to energy changes as the host material is changed. This insensitivity is a consequence of the closely similar electronegativity of all the III-V semiconductors. It is the insensitivity of the charge transfer to the host material that provides for the defect stability. This explanation stands in contrast to previous suggestions[8,22] which implied that the alignment of the transition-metal energy levels is a consequence of U much larger than the interaction energy between transition metal levels and the hybrids. Our results point out the role of the hybridization effect in weakening the effective intra-atomic Coulomb interaction are consistent with results obtained by Zunger.[7] Also, because U is included in a more realistic manner than in previously reported calculations,[8] we obtain predictions of chemical trends in the defect stability. The light transiton metals, such as Ti, exhibit excellent stability and should provide accurate reference levels for predicting band offsets and deformation potentials. On the other hand, it is found that the heavier transition-metal elements, such as Ni, hybridize less strongly with the host than the lighter transition metals and are more sensitive to changes in the host semiconductor.

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APPENDIX

The matrices S_1 to S_7 defined in II B are as follows:

$$\underline{S}_1=\begin{bmatrix} f_1 & 0 & 0 & 0\\ 0 & f_2 & 0 & 0\\ 0 & 0 & f_2 & 0\\ 0 & 0 & 0 & f_2\end{bmatrix},\quad \underline{S}_2=\begin{bmatrix} f_3 & f_4 & f_5 & f_4\\ f_4 & f_6 & f_8 & f_7\\ f_5 & f_8 & f_9 & -f_8\\ f_4 & f_7 & -f_8 & f_6\end{bmatrix},\quad \underline{S}_3=\begin{bmatrix} f_3 & f_5 & f_4 & f_4\\ f_5 & f_9 & -f_8 & -f_8\\ f_4 & -f_8 & f_6 & f_7\\ f_4 & -f_8 & f_7 & f_6\end{bmatrix},\quad \underline{S}_4=\begin{bmatrix} f_3 & f_4 & f_4 & f_5\\ f_4 & f_6 & f_7 & f_8\\ f_4 & f_7 & f_6 & f_8\\ f_5 & f_8 & f_8 & f_9\end{bmatrix},$$

$$\underline{S}_5=\begin{bmatrix} f_3 & -f_4 & f_4 & -f_5\\ -f_4 & f_6 & -f_7 & f_8\\ f_4 & -f_7 & f_6 & -f_8\\ -f_5 & f_8 & -f_8 & f_9\end{bmatrix},\quad \underline{S}_6=\begin{bmatrix} f_3 & -f_5 & f_4 & -f_4\\ -f_5 & f_9 & f_8 & -f_8\\ f_4 & f_8 & f_6 & -f_7\\ -f_4 & -f_8 & -f_7 & f_6\end{bmatrix},\quad \underline{S}_7=\begin{bmatrix} f_3 & f_4 & -f_5 & -f_4\\ f_4 & f_6 & -f_8 & -f_7\\ -f_5 & -f_8 & f_9 & -f_8\\ -f_4 & -f_7 & -f_8 & f_6\end{bmatrix},$$

$$f_1=48A_s^*A_s\ ,$$

$$f_1=48A_s^*A_s\ ,$$

$$f_2=16A_x^*A_x+A_y^*A_y+A_z^*A_z\ ,$$

$$f_3=16A_s^*A_s(\cos\rho_x\cos\rho_y+\cos\rho_y\cos\rho_z+\cos\rho_x\cos\rho_z)\ ,$$

$$\begin{aligned}f_4=8[&\varphi(A_s,A_x)(\sin\rho_x\cos\rho_y+\sin\rho_x\cos\rho_z)\\&+\varphi(A_s,A_y)(\sin\rho_y\cos\rho_x+\sin\rho_y\cos\rho_z)\\&+\varphi(A_s,A_z)(\sin\rho_z\cos\rho_x+\sin\rho_z\cos\rho_y)]\ ,\end{aligned}$$

$$\begin{aligned}f_5=-16[&\psi(A_s,A_x)\sin\rho_y\sin\rho_z+\psi(A_s,A_y)\sin\rho_x\cos\rho_z\\&+\psi(A_s,A_z)\sin\rho_x\sin\rho_y]\ ,\end{aligned}$$

$$\begin{aligned}f_6=8[&A_x^*A_x(\cos\rho_x\cos\rho_y+\cos\rho_x\cos\rho_z)\\&+A_y^*A_y(\cos\rho_y\cos\rho_x+\cos\rho_y\cos\rho_z)\\&+A_z^*A_z(\cos\rho_z\cos\rho_x+\cos\rho_z\cos\rho_y)]\ ,\end{aligned}$$

$$\begin{aligned}f_7=-16[&\psi(A_x,A_y)\sin\rho_x\sin\rho_y+\psi(A_x,A_z)\sin\rho_x\sin\rho_z\\&+\psi(A_y,A_z)\sin\rho_y\sin\rho_z]\ ,\end{aligned}$$

$$\begin{aligned}f_8=8[&\varphi(A_x,A_y)(\sin\rho_z\cos\rho_x-\sin\rho_z\cos\rho_y)\\&+\varphi(A_x,A_z)(\sin\rho_y\cos\rho_x-\sin\rho_y\cos\rho_z)\\&+\varphi(A_y,A_z)(\sin\rho_x\cos\rho_y-\sin\rho_x\cos\rho_z)]\ ,\end{aligned}$$

$$\begin{aligned}f_9=16[&A_x^*A_x\cos\rho_y\cos\rho_z+A_y^*A_y\cos\rho_x\cos\rho_z\\&+A_z^*A_z\cos\rho_x\cos\rho_y]\ ,\end{aligned}$$

$$\rho_x=k_xa/2,\quad \rho_y=k_ya/2,\quad \rho_z=k_za/2\ ,$$

$$\varphi(A_i,A_j)=\mathrm{Im}(A_j)\mathrm{Re}(A_i)-\mathrm{Im}(A_i)\mathrm{Re}(A_j)\ ,$$

$$\psi(A_i,A_j)=\mathrm{Re}(A_i)\mathrm{Re}(A_j)+\mathrm{Im}(A_i)\mathrm{Im}(A_j)\ .$$

The A_j are anion parts of eigenvectors written above as $A_\alpha^n(\mathbf{k})$.

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