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Two-center formulation of Mn^{2+}-electron *s-d* exchange coupling in bulk and quantum-confined diluted magnetic semiconductors

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Magnetic exchange coupling between Mn^{2+} spins and conduction-band electrons in diluted magnetic semiconductors (DMSs) is formulated in terms of a two-center kinetic-exchange process involving the empty Mn^{2+} 4*s* orbital. This formulation allows interpretation of the sign and magnitude of the *s-d* coupling in terms of specific interorbital transfer integrals and charge-transfer energies for the first time, similar to established approaches for interpreting *p-d* and *d-d* exchange energies in the same materials. This formulation allows recent proposals of dominant confinement-induced antiferromagnetic *s-d* exchange in DMS nanostructures to be assessed critically.

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$Mn^{2+}(3d)$-conduction-band (CB) electron (e^-_{CB}) exchange coupling in diluted magnetic semiconductors (DMSs) is sufficiently strong to induce sizable spin currents[1] and fast electron-spin relaxation[2] in $Cd_{1-x}Mn_xTe$ quantum wells, to overcome antiferromagnetic dimer pairing in $Zn_{1-x}Mn_xO$ quantum dots,[3] and to generate spin-polarized electrical currents in $Zn_{1-x}Mn_xSe$-containing spin-based light-emitting diodes,[4] yet its microscopic origins have not been clearly established. Whereas both Mn^{2+}-valence-band (VB) hole (h^+_{VB}) and Mn^{2+}-Mn^{2+} exchange interactions in DMSs have been formulated using perturbative expressions that allow successful interpretation of their signs and magnitudes in terms of basic features of the dopant and semiconductor geometric and electronic structures,[5,6] a similar formulation has not been developed for Mn^{2+}-e^-_{CB} exchange coupling. Instead, Mn^{2+}-e^-_{CB} exchange interactions in bulk DMSs are commonly described as examples of "potential exchange," in which the *s*-like $k=0$ band electrons and $Mn^{2+}(3d)$ electrons adopt parallel spin orientations to reduce their repulsive Coulomb interaction energy. The interaction is typically formulated using a Kondo-type Hamiltonian with a phenomenological coupling parameter, J_{sd}.[6,7] Such a description does not allow Mn^{2+}-e^-_{CB} exchange energies to be quantified in a transparent and intuitive fashion, and therefore does not allow ready prediction about their possible change with quantum confinement. With growing interest in spin effects in DMS nanostructures,[8–12] including solution-processable DMS nanocrystals,[3,13–18] the fundamental nature of the *s-d* exchange interaction and its dependence on quantum confinement have become the subject of renewed attention and debate. In this paper, we present a perturbative formulation of the Mn^{2+}-e^-_{CB} exchange energies of bulk DMSs. This description is grounded in historically established two-center exchange-coupling formalisms[19,20] but to our knowledge has not previously been used to describe Mn^{2+}-e^-_{CB} exchange coupling in DMSs. Changes in Mn^{2+}-e^-_{CB} exchange due to quantum confinement in DMS nanostructures are then discussed in light of this formulation.

By analogy to descriptions of Mn^{2+}-h^+_{VB} exchange (kinetic *p-d* exchange),[5,6] we first define the wave functions of the spins that will be coupled. For brevity, the discussion is restricted to the idealized case of Mn^{2+} in a cubic II-VI lattice but the formalism is readily generalized. For this case, the five Mn^{2+} spins are distributed in the 3*d* orbitals to yield a high-spin orbital singlet ($^6A_1$) ground term. To first order, the e^-_{CB} wave function is described by a $k=0$ Bloch function composed primarily of cation *s* orbitals but with substantial anion *p* character. As is frequently noted,[7,21–23] hybridization of this *s*-like e^-_{CB} wave function with the Mn^{2+} 3*d* orbitals is forbidden by symmetry. For this reason, antiferromagnetic kinetic *s-d* exchange (of the type dominant in *p-d* exchange) is also forbidden by symmetry in bulk semiconductors at $k=0$, leaving just the ferromagnetic so-called "potential *s-d* exchange" as the only remaining coupling mechanism.[7,21–23] Here, we recast this bulk ferromagnetic *s-d* exchange interaction in terms of microscopic two-center kinetic-exchange processes.

To illustrate the microscopic Mn^{2+}-semiconductor orbital interactions we will invoke, Fig. 1(a) depicts a qualitative molecular-orbital (MO) diagram constructed from the valence orbitals of the Mn^{2+} (3*d*,4*s*,4*p*) and the semiconductor

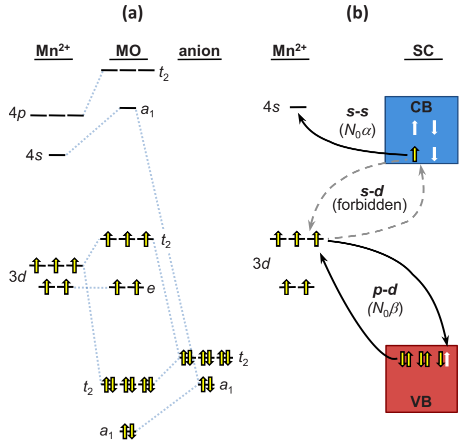

FIG. 1. (Color online) (a) Molecular-orbital diagram for a Mn^{2+} cation (3*d*, 4*s*, and 4*p* orbitals on the left) interacting with four σ-donor anions (a_1 and t_2 SALCs of sp^3 hybridized orbitals on the right) in tetrahedral (T_d) symmetry. (b) Schematic overview of the relevant two-center exchange pathways in DMSs (SC = semiconductor).

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anions [$n(s,p)$, where $n=2(\mathrm{O}^{2-})$, $3(\mathrm{S}^{2-})$, $4(\mathrm{Se}^{2-})$, or $5(\mathrm{Te}^{2-})$] within the T_d point symmetry of the Mn^{2+} site. sp^3 hybridization of the anion valence orbitals is assumed, generating one donor orbital (dangling bond) from each that is available for bonding to the Mn^{2+}. In T_d symmetry, these anion orbitals combine to form a_1 and t_2 symmetry-adapted linear combinations (SALCs). The same anion valence orbitals make the major contribution to the VB Bloch functions of the extended lattice [Fig. 1(b)]. In T_d symmetry, the five Mn^{2+} d orbitals transform as the well-known e and t_2 sets, the latter having appropriate symmetry to interact with the t_2 SALC of anion orbitals. The empty Mn^{2+} $4p$ orbitals also transform as t_2 symmetry and overlap more with the anion t_2 set than the d orbitals do because of their greater radial extension but occur at higher energy. The Mn^{2+} $4s$ orbital has a_1 symmetry and interacts strongly with the anion SALC of a_1 symmetry. For our purposes, it is acceptable to neglect Mn^{2+} $3d$-$4p$ hybridization, which is allowed by symmetry in the T_d point group. Importantly, Fig. 1(a) illustrates that the orbital interaction predominantly responsible for the favorable thermodynamics of Mn^{2+}-anion bond formation involves the empty Mn^{2+} $4s$ orbital. This local MO diagram will guide the microscopic description of Mn^{2+}-e^-_CB exchange pathways presented below.

Following Goodenough,[19] and Weihe and Güdel,[20] experimental two-center exchange energies may have various kinetic and potential exchange contributions. Whereas potential exchange is always ferromagnetic, kinetic-exchange pathways can be either antiferromagnetic or ferromagnetic. Although often weaker than their antiferromagnetic counterparts, ferromagnetic kinetic-exchange interactions are ubiquitous in magnetic materials and can even dominate the overall coupling in some cases, for instance, double-exchange interactions in solids and molecules.[24–27] A well-known example of ferromagnetic kinetic exchange in DMSs is the Cr-Cr superexchange interaction of Cr(II)-doped II-VI semiconductors.[6,28] The simplest case of ferromagnetic kinetic exchange involves spin-dependent partial electron transfer from a half-filled orbital on one center (a) into an empty orbital on a second center (b) that also contains unpaired electrons in its other orbitals. The energy associated with this type of kinetic-exchange pathway is described by Eq. (1),[20]

$$J_{KE}^{ab}(\text{half filled, empty}) = \frac{V_{ab}^2}{4S_a(S_b+1/2)}\,\frac{I_{intra}}{E_{a\to b\uparrow}\times E_{a\to b\downarrow}}. \tag{1}$$

I_{intra} is the intraion exchange energy, which favors high-spin multiplicities, V_{ab} is the so-called transfer (or hopping) integral, S_a and S_b are the spins of centers a and b, and $E_{a\to b}$ is the energy required to transfer an electron from center a to center b with the indicated spin.

We propose that precisely this kinetic-exchange scenario can be used to describe the ferromagnetic Mn^{2+}-e^-_CB exchange coupling in DMSs that is typically referred to as "potential s-d exchange." Placement of an unpaired electron in the CB of a II-VI lattice generates spin density primarily on the group-II cations but also partially on the group-VI anions in inverse proportion to the lattice ionicity. Some of this spin density is on the anions forming the a_1 SALC that interacts covalently with the Mn^{2+} $4s$ orbital [Fig. 1(a)]. The transfer of spin density from this a_1 SALC to the Mn^{2+} $4s$ orbital thus constitutes a ferromagnetic kinetic-exchange process describable using Eq. (1). Formally, the relevant kinetic-exchange virtual transition involves the transfer of e^-_CB into the Mn^{2+} $4s$ orbital to form Mn^+ in its $3d^54s^1$ configuration [Fig. 1(b)]. Importantly, the free Mn^+ ion has a high-spin ^{7}S ($3d^54s^1$) ground state that is stabilized by $I_{intra}^{free\ ion}\sim 1.2$ eV relative to the intermediate-spin ^{5}S ($3d^54s^1$) state.[29] Through configuration interaction, this energy ordering in Mn^+ $3d^54s^1$ states (which are charge-transfer excited states of the Mn^{2+}-e^-_CB pair) leads to stabilization of the high-spin configuration of the Mn^{2+}-e^-_CB pair in its ground state, by an energy given by Eq. (1). In the free ion, the first Mn^+ state having a $3d^6$ configuration occurs $\sim$1.8 eV above the ^{7}S ($3d^54s^1$) ground state (Fig. 2).[29] Mn^+ retains its ^{7}S ($3d^54s^1$) ground state in crystals such as SrCl_2[30] and NaCl,[31] and the empty Mn^{2+} $4s$ orbital is expected to be lower in energy than the empty $3d\!\downarrow$ orbitals in Mn^{2+}-doped II-VI semiconductors, as well (Fig. 2).

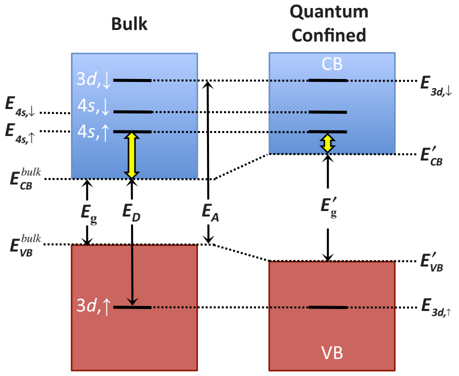

FIG. 2. (Color online) Energy levels in bulk and quantum-confined DMSs, including the $3d$-based donor ($\mathrm{Mn}^{2+/3+}, E_{3d,\uparrow}$) and acceptor ($\mathrm{Mn}^{2+/+}, E_{3d,\downarrow}$) levels of Mn^{2+}, assumed fixed relative to vacuum. The yellow arrows show the energy spacings relevant to Mn^{2+}-e^-_CB exchange.

With this approach, the DMS mean-field Mn^{2+}-e^-_CB exchange parameter $N_0\alpha$ can now be formulated in terms of fundamental dopant and semiconductor geometric and electronic structure parameters as shown in Eq. (2),

$$N_0\alpha = 2J_{KE}^{ss} = \frac{V_{ss}^2}{(S_\mathrm{Mn}+1/2)}\,\frac{I_{intra}}{(E_{4s\uparrow}-E_\mathrm{CB})(E_{4s\downarrow}-E_\mathrm{CB})}. \tag{2}$$

The parameters used in these calculations were determined as described below and are all summarized in Table I. The kinetic s-s transfer integrals V_{ss} were estimated using Harrison's tight-binding approach as in Eq. (3), where d is the distance between the two interacting orbitals, and $\hbar^2/m = 7.62$ eV Å^2,[54]

$$V_{ss} = -5.6\frac{\hbar^2}{m}\frac{c}{d^2}. \tag{3}$$

The constant c accounts for the lattice ionicity, f_i (i.e., the fact that only a fraction of the e^-_CB spin density resides on the

TABLE I. Calculated and experimental exchange interaction parameters for different Mn^{2+}-doped II-VI semiconductors. Idealized cubic symmetries and a value of $I_{intra}=0.84$ eV were used throughout.

	CdMnTe	CdMnSe	CdMnS	ZnMnTe	ZnMnSe	ZnMnS	ZnMnO
f_i (%)[a]	76	78	78	76	78	78	90
d (Å)	2.759[b]	2.572[b]	2.453[b]	2.722[b]	2.533[b]	2.411[b]	1.990[c]
E_D (eV)	5.2	4.8[d]	5.0	6.2	5.6	6.1	5.3
E_A (eV)	5.3	6.0	6.5	5.2	6.1	6.6	7.1
E_g (eV)[e]	1.5	1.8	2.5	2.4	2.7	3.7	3.4
$E_{4s\uparrow}-E_{\mathrm{CB}}$ (eV)	2.2	2.6	2.4	1.2	1.8	1.4	2.1
V_{ss} (eV)	−1.94	−2.14	−2.35	−2.00	−2.21	−2.43	−2.41
V_{pd} (eV)	−2.20	−2.50	−2.87	−2.45	−2.59	−3.21	−3.36
$N_0\alpha^{calc}$ (eV)	0.16	0.14	0.21	0.46	0.29	0.56	0.26
$N_0\alpha^{exp}$ (eV)	0.22[f]	0.261[g] 0.258[h] 0.2574[i]	0.22[j]	0.19[k]	0.29[l] 0.26[m]		
$N_0\beta^{calc}$ (eV)	−0.89	−1.25	−1.80	−1.09	−1.37	−2.37	−3.02
$N_0\beta^{exp}$ (eV)	−0.88[n]	$-1.238(x)$[i] $-1.301(z)$[i]	−1.80[o]	−1.09[k]	−1.4[l] −1.31[m]		
J_{dd}^{calc} (meV)	−0.35	−0.41	−0.59	−0.56	−0.46	−0.86	−0.88
J_{dd}^{exp} (meV)	−0.53[p] −0.54[q]	−0.68[q] −0.70[r]	−0.74[s] −0.90[p] −0.91[r]	−0.757[t] −0.797[u] −0.820[v]	−0.85[s] −1.06[v] −1.09[p]	−1.39[v]	−1.64[w]

[a] Reference 32.
[b] Reference 5.
[c] Reference 33.
[d] References 34 and 35.
[e] Reference 36.
[f] Reference 37.
[g] Reference 38.
[h] Reference 39.
[i] Reference 40.
[j] Reference 41.
[k] Reference 42.
[l] Reference 43.
[m] Reference 44.
[n] Reference 37.
[o] Reference 45.
[p] Reference 46.
[q] Reference 47.
[r] Reference 48.
[s] Reference 49.
[t] Reference 50.
[u] Reference 51.
[v] Reference 52.
[w] Reference 53.

group-VI anions), as described by Eq. (4), and is known experimentally,[32]

$$c=\sqrt{(1-f_i)/2}. \tag{4}$$

I_{intra} is reduced from its free ion value by covalency (nephelauxetic effect), and is approximated here as $\sim 0.7 I_{intra}^{free\ ion}$ for all lattices. By definition, $I_{intra}=E_{4s\downarrow}-E_{4s\uparrow}$.

The charge-transfer energies E_D and E_A are related to the energies of the donor ($\mathrm{Mn}^{2+/3+}, E_{3d,\uparrow}$) and acceptor ($\mathrm{Mn}^{2+/+}, E_{3d,\downarrow}$) levels of the Mn^{2+} dopant, respectively (Fig. 2). The energy difference between those two levels is related to the effective Hubbard energy (U_{eff}) as in Eq. (5),[55]

$$U_{eff}=E_{3d\downarrow}-E_{3d\uparrow}=E_A+E_D-E_g. \tag{5}$$

Although U_{eff} is expected to vary somewhat from lattice to lattice, for the purposes of this paper we fix its value to 9 eV for all lattices in order to minimize adjustable variables.

Following the internal-reference rule,[56–60] the absolute positions of the donor and acceptor levels were also approximated to be independent of the lattice. This condition imposes constraints on the relative values of E_A and E_D across the II-VI series. The valence-band edge of CdSe was fixed at 3.0 eV above the Mn^{2+} donor level (i.e., $E_D=E_g+3.0$ eV $=4.8$ eV, Table I), in agreement with photoemission data.[34,35] The alignment of the other II-VI semiconductors relative to CdSe was then approximated from the band offsets proposed by Langer and Heinrich for the II-VI chalcogenide semiconductors,[59,60] which are similar to the universal offsets more recently proposed by Van de Walle.[61,62] This approach determines uniquely the values of E_A and E_D for each material, as given in Table I. The ZnO valence-band edge was fixed at −1.1 eV relative to the CdSe valence-band edge, consistent with the experimental offset reported in Ref. 63, although it has been suggested more recently that $\mathrm{Zn}_{1-x}\mathrm{Mn}_x\mathrm{O}$ may be anomalous among Mn^{2+}-based II-VI DMSs in not possessing an inverted bonding scheme.[64] $N_0\alpha$ values calculated using the above approach are summarized in Table I and discussed below.

Importantly, $N_0\beta$ and J_{dd} can also be calculated using similar perturbation formulas [Eqs. (6) and (7)][5,65,66] that rely on a common set of parameters,[67]

$$N_0\beta=-\frac{V_{pd}^2}{S_{\mathrm{Mn}}}\left(\frac{1}{E_D-E_g}+\frac{1}{E_A}\right), \tag{6}$$

$$J_{dd}=-\frac{V_{pd}^4}{S_{\mathrm{Mn}}^2}\left[\frac{1}{E_A^2(E_A+E_D-E_g)}+\frac{1}{E_A^3}\right]\frac{f(r)}{512}. \tag{7}$$

Here, V_{pd} is the $\mathrm{Mn}^{2+}(3d)$-h_{VB}^{+} transfer integral, $f(r)$ is a dimensionless constant equal to 4.4 for nearest-neighbor d-d

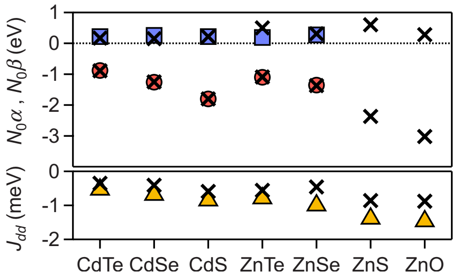

FIG. 3. (Color online) Comparison of calculated (×) and experimental ($N_0\alpha$:■, $N_0\beta$:●, and J_{dd}:▲) values for the exchange energies of Mn^{2+}-doped II-VI semiconductors. See text and Table I for details.

interactions,[5] and the energy parameters are defined in Fig. 2. V_{pd} was the only adjustable parameter and was adjusted to best reproduce the experimental numbers. ZnO aside, the values obtained for V_{pd} follow the expected $d^{-7/2}$ scaling.[54] The results of these calculations are also summarized in Table I, along with the $N_0\alpha$ results.

To illustrate these results, Fig. 3 plots all three calculated exchange energies across the entire series of Mn^{2+}-based II-VI DMSs, and compares them with available experimental energies. For all lattices, all three calculated exchange energies agree reasonably well with their experimental values. The calculated $N_0\alpha$ and $N_0\beta$ values are all within ± 0.15 eV of experiment and the calculated J_{dd} values are all within ± 0.5 meV of experiment. Equation (2) thus correctly reproduces both the sign and magnitude of $N_0\alpha$ using parameters that also reproduce the experimental values of $N_0\beta$ and J_{dd}, and we conclude that it correctly captures the microscopic essence of the Mn^{2+}-e^-_{CB} exchange interaction. The merit of this two-center formulation of Mn^{2+}-e^-_{CB} exchange is its grounding in the same perturbation approach as already widely used to describe Mn^{2+}-h^+_{VB} and Mn^{2+}-Mn^{2+} exchange:[5,6] $N_0\alpha$ can now be understood in terms of simple charge-transfer energies and transfer integrals in parallel with the way $N_0\beta$ and J_{dd} are presently understood. For the first time, all three commonly measured exchange energies of DMSs can thus be calculated using the same general perturbation approach.

One area where this two-center formulation is particularly helpful is in understanding the effects of quantum confinement on $N_0\alpha$. It has been shown that confinement relaxes the symmetry forbiddenness of antiferromagnetic kinetic *s*-*d* exchange found in bulk DMSs by reducing the symmetry of the e^-_{CB} wave function.[23] The resulting confinement-induced kinetic *s*-*d* exchange interaction has also been formulated using perturbation theory, and can be expressed as in Eq. (8),[23]

$$2J^{sd}_{KE} = -\frac{V^2_{sd}}{S_{\mathrm{Mn}}}\left(\frac{1}{E_{3d\downarrow} - E_{\mathrm{CB}}} + \frac{1}{E_D}\right). \tag{8}$$

Although the group theoretical basis for confinement-induced kinetic *s*-*d* exchange is established, its experimental magnitude remains debated. Specifically, it is not yet clear whether the kinetic *s*-*d* transfer integral (V_{sd}) can ever become sufficiently different from zero to be experimentally significant. Several recent publications have claimed observation of antiferromagnetic kinetic *s*-*d* exchange effects[15,16,23,68,69] but other recent spectroscopic results on colloidal doped quantum dots have raised doubts about this possibility.[18] Because the normal [Eq. (2)] and confinement-induced [Eq. (8)] contributions to the Mn^{2+}-e^-_{CB} exchange energy can now both be described by perturbation expressions, it is possible to estimate quantitatively the threshold condition for observation of dominant kinetic *s*-*d* exchange. From Eqs. (2) and (8), antiferromagnetic kinetic *s*-*d* exchange will surpass the normal ferromagnetic kinetic *s*-*s* exchange only when the condition of Eq. (9) is met,

$$\left|\frac{V^2_{sd}}{S_{\mathrm{Mn}}}\left(\frac{1}{E_{3d\downarrow} - E_{\mathrm{CB}}} + \frac{1}{E_D}\right)\right| \geq \left|\frac{V^2_{ss}}{(S_{\mathrm{Mn}} + 1/2)}\frac{I_{intra}}{(E_{4s\uparrow} - E_{\mathrm{CB}})(E_{4s\downarrow} - E_{\mathrm{CB}})}\right|. \tag{9}$$

Entering literature parameters (Table I), $N_0\alpha$ will become negative only for $V_{sd} > \sim V_{ss}/2$. Achieving this condition experimentally appears implausible, however, because V_{ss} is large [the dominant cation-anion bonding interaction, Fig. 1(a)], whereas V_{sd} is zero by symmetry to first order. Given this relationship, we expect the antiferromagnetic kinetic *s*-*d* exchange of Eq. (8) to remain small relative to the ferromagnetic kinetic exchange of Eq. (2) under all circumstances. Previous treatments have argued that kinetic *s*-*d* exchange may become large and even dominant when confinement narrows the energy gap between the CB edge and the $\mathrm{Mn}^{2+/+}(3d^5\text{-}3d^6)$ acceptor level because this reduces the virtual transition energy $E_{3d\downarrow} - E_{\mathrm{CB}}$ in Eq. (8).[15,23] From Fig. 2 and Eq. (9), however, it is apparent that confinement also reduces $E_{4s} - E_{\mathrm{CB}}$ and therefore also enhances the normal ferromagnetic Mn^{2+}-e^-_{CB} exchange [Eq. (2)]. The concomitant increase in ferromagnetic Mn^{2+}-e^-_{CB} exchange-coupling strength with confinement is not obvious from the usual description of this interaction as "potential *s*-*d* exchange," and indeed was neglected in previous treatments, but it becomes apparent from the two-center formulation of Eq. (2). Advances in density-functional theory (DFT) methodologies now allow model-free assessment of such *sp*-*d* exchange interactions in magnetic semiconductors.[70] Although more studies are needed, DFT calculations on II-VI semiconductor nanostructures appear to show no evidence of antiferromagnetic *s*-*d* exchange, even in the strong confinement regime,[3,71] providing independent support of the above conclusion. Overall, the analysis here suggests that $N_0\alpha$ will likely scale in proportion with the $\mathrm{Mn}^{2+}(4s)$ character of the e^-_{CB} wave function for all Mn^{2+}-based DMSs, regardless of quantum confinement.

In summary, a perturbation expression has been presented that describes Mn^{2+}-e^-_{CB} magnetic exchange coupling as arising from a two-center ferromagnetic kinetic *s*-*s* exchange interaction. In contrast with other descriptions of Mn^{2+}-e^-_{CB} exchange, this formulation allows the sign and magnitude of $N_0\alpha$ to be calculated from basic geometric and electronic-structure parameters within the same perturbation formalism as already widely and successfully applied to calculate the related parameters $N_0\beta$ and J_{dd} in various DMSs. Application of this two-center formulation allows the microscopic aspects of Mn^{2+}-e^-_{CB} exchange in DMS nanostructures to be evaluated, and suggests that neither the primary nature of the fundamental exchange interaction nor its sign should change upon introduction of quantum confinement.

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[1] S. D. Ganichev, S. A. Tarasenko, V. V. Bel'kov, P. Olbrich, W. Eder, D. R. Yakovlev, V. Kolkovsky, W. Zaleszczyk, G. Karczewski, T. Wojtowicz, and D. Weiss, Phys. Rev. Lett. **102**, 156602 (2009).

[2] C. Camilleri, F. Teppe, D. Scalbert, Y. G. Semenov, M. Nawrocki, M. Dyakonov, J. Cibert, S. Tatarenko, and T. Wojtowicz, Phys. Rev. B **64**, 085331 (2001).

[3] S. T. Ochsenbein, Y. Feng, K. M. Whitaker, E. Badaeva, W. K. Liu, X. Li, and D. R. Gamelin, Nature Nanotech. **4**, 681 (2009).

[4] B. T. Jonker, Y. D. Park, B. R. Bennett, H. D. Cheong, G. Kioseoglou, and A. Petrou, Phys. Rev. B **62**, 8180 (2000).

[5] B. E. Larson, K. C. Hass, H. Ehrenreich, and A. E. Carlsson, Phys. Rev. B **37**, 4137 (1988).

[6] P. Kacman, Semicond. Sci. Technol. **16**, R25 (2001).

[7] *Diluted Magnetic Semiconductors*, edited by J. K. Furdyna and J. Kossut (Academic, New York, 1988).

[8] A. A. Maksimov, G. Bacher, A. McDonald, V. D. Kulakovskii, A. Forchel, C. R. Becker, G. Landwehr, and L. W. Molenkamp, Phys. Rev. B **62**, R7767 (2000).

[9] J. Seufert, G. Bacher, M. Scheibner, A. Forchel, S. Lee, M. Dobrowolska, and J. K. Furdyna, Phys. Rev. Lett. **88**, 027402 (2001).

[10] L. Besombes, Y. Léger, L. Maingault, D. Ferrand, H. Mariette, and J. Cibert, Phys. Rev. Lett. **93**, 207403 (2004).

[11] G. Bacher, H. Schömig, M. Scheibner, A. Forchel, A. A. Maksimov, A. V. Chernenko, P. S. Dorozhkin, V. D. Kulakovskii, T. Kennedy, and T. L. Reinecke, Physica E **26**, 37 (2005).

[12] A. V. Chernenko, A. S. Brichkin, N. A. Sobolev, and M. C. Carmo, J. Phys.: Condens. Matter **22**, 355306 (2010).

[13] R. Beaulac, S. T. Ochsenbein, and D. R. Gamelin, in *Semiconductor Quantum Dots*, edited by V. I. Klimov (CRC, Boca Raton, 2010), p. 397.

[14] R. Beaulac, L. Schneider, P. I. Archer, G. Bacher, and D. R. Gamelin, Science **325**, 973 (2009).

[15] D. A. Bussian, S. A. Crooker, M. Yin, M. Brynda, Al. L. Efros, and V. I. Klimov, Nature Mater. **8**, 35 (2009).

[16] J. H. Yu, X. Liu, K. E. Kweon, J. Joo, J. Park, K.-T. Ko, D. W. Lee, S. Shen, K. Tivakornsasithorn, J. S. Son, J.-H. Park, Y.-W. Kim, G. S. Hwang, M. Dobrowolska, J. K. Furdyna, and T. Hyeon, Nature Mater. **9**, 47 (2010).

[17] Z. Li, L. Cheng, Q. Sun, Z. Zhu, M. J. Riley, M. Aljada, Z. Cheng, X. Wang, G. R. Hanson, S. Qiao, S. C. Smith, and G. Q. Lu, Angew. Chem. **49**, 2777 (2010).

[18] V. A. Vlaskin, R. Beaulac, and D. R. Gamelin, Nano Lett. **9**, 4376 (2009).

[19] J. B. Goodenough, *Magnetism and the Chemical Bond* (Wiley, New York, 1963).

[20] H. Weihe and H. U. Güdel, Inorg. Chem. **36**, 3632 (1997).

[21] Yu. G. Semenov and B. D. Shanina, Phys. Status Solidi B **104**, 631 (1981).

[22] A. K. Bhattacharjee, G. Fishman, and B. Coqblin, Physica B **117-118**, 449 (1983).

[23] I. A. Merkulov, D. R. Yakovlev, A. Keller, W. Ossau, J. Geurts, A. Waag, G. Landwehr, G. Karczewski, T. Wojtowicz, and J. Kossut, Phys. Rev. Lett. **83**, 1431 (1999).

[24] P. W. Anderson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 1, p. 25.

[25] D. R. Gamelin, E. L. Bominaar, M. L. Kirk, K. Wieghardt, and E. I. Solomon, J. Am. Chem. Soc. **118**, 8085 (1996).

[26] G. Blondin and J.-J. Girerd, Chem. Rev. **90**, 1359 (1990).

[27] C. Zener, Phys. Rev. **82**, 403 (1951).

[28] J. Blinowski, P. Kacman, and J. A. Majewski, J. Cryst. Growth **159**, 972 (1996).

[29] C. Corliss and J. Sugar, J. Phys. Chem. Ref. Data **6**, 1253 (1977).

[30] V. M. Orera, P. J. Alonso, R. Cases, and R. Alcala, Radiat. Eff. **83**, 213 (1984).

[31] M. Ikeya and N. Itoh, J. Phys. Chem. Solids **32**, 2569 (1971).

[32] O. Matumura, J. Phys. Soc. Jpn. **14**, 108 (1959).

[33] E. Chikoidze, Y. Dumont, H. J. von Bardeleben, W. Pacuski, and O. Gorochov, Superlattices Microstruct. **42**, 176 (2007).

[34] A. Franciosi, S. Chang, R. Reifenberger, U. Debska, and R. Riedel, Phys. Rev. B **32**, 6682 (1985).

[35] B. A. Orlowski, K. Kopalko, and W. Chab, Solid State Commun. **50**, 749 (1984).

[36] O. Madelung, *Semiconductors: Data Handbook*, 3rd ed. (Springer, Berlin, 2004).

[37] J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).

[38] Y. Shapira, D. Heiman, and S. Foner, Solid State Commun. **44**, 1243 (1982).

[39] D. Heiman, Y. Shapira, S. Foner, B. Khazai, R. Kershaw, K. Dwight, and A. Wold, Phys. Rev. B **29**, 5634 (1984).

[40] M. Arciszewska and M. Nawrocki, J. Phys. Chem. Solids **47**, 309 (1986).

[41] D. Heiman, Y. Shapira, and S. Foner, Solid State Commun. **45**, 899 (1983).

[42] A. Twardowski, P. Swiderski, M. von Ortenberg, and R. Pauthenet, Solid State Commun. **50**, 509 (1984).

[43] A. Twardowski, T. Dietl, and M. Demianiuk, Solid State Commun. **48**, 845 (1983).

[44] A. Twardowski, M. von Ortenberg, M. Demianiuk, and R. Pauthenet, Solid State Commun. **51**, 849 (1984).

[45] M. Nawrocki, J. P. Lascaray, D. Coquillat, and M. Demianiuk, *Diluted Magnetic (Semimagnetic) Semiconductors*, MRS Symposia Proceedings No. 89 (Materials Research Society, Pittsburgh, 1987), p. 65.

[46] Y. Shapira and N. F. Oliveira, Phys. Rev. B **35**, 6888 (1987).

[47] B. E. Larson, K. C. Hass, and R. L. Aggarwal, Phys. Rev. B **33**, 1789 (1986).

[48] D. U. Bartholomew, E. K. Suh, S. Rodriguez, A. K. Ramdas, and R. L. Aggarwal, Solid State Commun. **62**, 235 (1987).

[49] J. P. Lascaray, M. Nawrocki, J. M. Broto, M. Rakoto, and M. Demianiuk, Solid State Commun. **61**, 401 (1987).

[50] L. M. Corliss, J. M. Hastings, S. M. Shapiro, Y. Shapira, and P. Becla, Phys. Rev. B **33**, 608 (1986).

[51] G. Barilero, C. Rigaux, N. Hy Hau, J. C. Picoche, and W. Giriat, Solid State Commun. **62**, 345 (1987).

[52] T. M. Giebultowicz, J. J. Rhyne, and J. K. Furdyna, J. Appl. Phys. **61**, 3537 (1987).

[53] S. Kolesnik, B. Dabrowski, Z. Q. Wiren, H. Kepa, T. M. Giebultowicz, C. M. Brown, J. Leao, and J. K. Furdyna, J. Appl. Phys. **99**, 08M122 (2006).

[54] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1989).

[55] J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963).

[56] M. J. Caldas, A. Fazzio, and A. Zunger, Appl. Phys. Lett. **45**, 671 (1984).

[57] A. Zunger, Annu. Rev. Mater. Sci. **15**, 411 (1985).

[58] A. Zunger, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1986), Vol. 39, p. 275.

[59] J. M. Langer, C. Delerue, M. Lannoo, and H. Heinrich, Phys. Rev. B **38**, 7723 (1988).

[60] J. M. Langer and H. Heinrich, Phys. Rev. Lett. **55**, 1414 (1985).

[61] C. G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).

[62] C. G. Van de Walle and J. Neugebauer, Annu. Rev. Mater. Res. **36**, 179 (2006).

[63] B. Carlson, K. Leschkies, E. S. Aydil, and X. Y. Zhu, J. Phys. Chem. C **112**, 8419 (2008).

[64] C. A. Johnson, K. R. Kittilstved, T. C. Kaspar, T. C. Droubay, S. A. Chambers, G. M. Salley, and D. R. Gamelin, Phys. Rev. B **82**, 115202 (2010).

[65] T. Mizokawa and A. Fujimori, Phys. Rev. B **48**, 14150 (1993).

[66] T. Chanier, F. Virot, and R. Hayn, Phys. Rev. B **79**, 205204 (2009).

[67] We note a difference in the definition of V_{pd} here from the work of Larson *et al.* (Ref. 5). The two constants are related as $V_{pd}^{Larson}=\frac{V_{pd}}{\sqrt{32}S_{\mathrm{Mn}}}$. This difference is the origin of the factor of 512 appearing in Eq. (7). Note, too, that Eqs. (1) and (7) are related to the Hamiltonian $\hat{H}=-2J\hat{S}_a\cdot\hat{S}_b$, whereas $N_0\alpha$ and $N_0\beta$ are both defined using the Hamiltonian $\hat{H}=-J\hat{S}_a\cdot\hat{S}_b$.

[68] R. C. Myers, M. Poggio, N. P. Stern, A. C. Gossard, and D. D. Awschalom, Phys. Rev. Lett. **95**, 017204 (2005).

[69] N. P. Stern, R. C. Myers, M. Poggio, A. C. Gossard, and D. D. Awschalom, Phys. Rev. B **75**, 045329 (2007).

[70] K. Sato, L. Bergqvist, J. Kudrnovsky, P. H. Dederichs, O. Eriksson, I. Turek, B. Sanyal, G. Bouzerar, H. Katayama-Yoshida, V. A. Dinh, T. Fukushima, H. Kizaki, and R. Zeller, Rev. Mod. Phys. **82**, 1633 (2010).

[71] C. Echeverría-Arrondo, J. Pérez-Conde, and A. Ayuela, Phys. Rev. B **79**, 155319 (2009).