

## Mapping of electronic wave functions in II-VI semiconductor quantum wells via $\text{Mn}^{2+}$ electron paramagnetic resonance

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(Received 16 February 1999; revised manuscript received 1 February 2000)

We examine the shift of the electron paramagnetic resonance of substitutional  $\text{Mn}^{2+}$  ions induced by exchange interaction with band electrons in a II-VI semiconductor quantum well. We show that such a shift is directly proportional to the local electron probability density which the  $\text{Mn}^{2+}$  ion “sees” at its specific site. Based on this, we demonstrate that  $\text{Mn}^{2+}$  ions can be used as built-in localized probes for mapping the spatial distribution of the wave function amplitudes of electronic states confined in the quantum well.

Semiconductor superlattices and other submicron heterostructures are of great theoretical and experimental interest both for their device potentials, and because of the fundamental physical phenomena that they exhibit due to their materials properties and their reduced dimensionality.<sup>1,2</sup> One aspect of such structures with important physical consequences is their ability to localize charge carriers on the nanometer scale. In a quantum well or a superlattice, this localization of carrier wave functions in the well regions determines both optical and transport properties of the structure. Thus, in order to understand the physical properties of semiconductor superlattices and quantum wells, it is important to have the ability to determine the spatial distribution of the wave functions in these structures. Many theoretical models have been developed for calculating the electronic wave functions in semiconductor heterostructures.<sup>1,3–5</sup> Determining the wave functions *experimentally* (i.e., probing the local charge density distribution in the heterostructures), however, still remains a major challenge.<sup>6</sup>

In this paper we show that  $\text{Mn}^{2+}$  ions can be used as built-in localized probes for mapping the wave functions of electronic states in II-VI semiconductor quantum wells. This approach is based on the effect described in Ref. 7, that the electron-paramagnetic-resonance EPR line of substitutional  $\text{Mn}^{2+}$  ions in a II-VI semiconductor will undergo a shift due to the spin-spin exchange interaction between the localized  $\text{Mn}^{2+}$  ions and band electrons. We will show that in a semiconductor *quantum well* such a shift is directly proportional to the local electronic probability density which the specific  $\text{Mn}^{2+}$  ion “sees” at its site. Since within a given quantum well the substitutional  $\text{Mn}^{2+}$  ions can occupy atomic positions only in certain discrete planes (with respect to the growth direction), the measurement of such resonance shifts provides a direct handle for determining the electron probability density distribution (i.e., for “mapping” the wave function amplitudes) in that quantum well.

For the purpose of illustration, let us consider a single quantum well bounded by the (001) crystallographic planes, as shown in Fig. 1, with  $\text{Mn}^{2+}$  ions in the well region. To be specific, we consider the situation where the Fermi level lies

between the ground state and the first excited state ( $E_1 < E_F < E_2$ ), as shown in Fig. 1, and we also assume that  $E_2 - E_F \gg kT$ . In this case the exchange Hamiltonian becomes<sup>7</sup>

$$H_{\text{ex}}(\mathbf{R}_j) = J(\mathbf{R}_j) \mathbf{S} \cdot \sum_{\mathbf{k}_{xy}, \gamma} \boldsymbol{\sigma}_{\mathbf{k}_{xy}, \gamma} f(\mathbf{k}_{xy}, T), \quad (1)$$

where  $\mathbf{S}$  is the spin operator for  $3\text{D}^5$  electrons of the  $\text{Mn}^{2+}$  ion located at the  $\mathbf{R}_j$  cation site, and  $\boldsymbol{\sigma}_{\mathbf{k}_{xy}, \gamma}$  is the spin operator for the electron occupying the  $\mathbf{k}_{xy}$  state ( $\mathbf{k}_{xy}$  is the wave vector in the  $xy$  plane) of the first subband,  $\gamma = +, -$  refers to spin-up and spin-down electron states, respectively, and  $f(\mathbf{k}_{xy}, T)$  is the Fermi distribution function.  $J(\mathbf{R}_j)$  represents the  $s$ - $d$  potential exchange integral between the  $\mathbf{S}$  and the  $\boldsymbol{\sigma}_{\mathbf{k}_{xy}, \gamma}$  spin states. Since the quantum well structure does not possess translational symmetry, the exchange integral in this case depends also on the atomic site  $\mathbf{R}_j$  occupied by the  $\text{Mn}^{2+}$  ion. However, from symmetry considerations it is easy to see that  $J(\mathbf{R}_j)$  is the same for all  $\text{Mn}^{2+}$  ions located in the same atomic layer perpendicular to the growth direction (i.e., at the same discrete value of  $z$  occupied by group-II atoms), so that it can be characterized by a group-II atomic layer index (a discrete integer)  $m$  in the quantum well instead of  $\mathbf{R}_j$ . We then have<sup>7</sup>

$$J(m) = -2 \int \int \mathbf{F}^*(z) u_c^{2d*}(\mathbf{r}) \phi_d^*(r') |{}_m \times V(\mathbf{r} - \mathbf{r}') F(z') u_c^{2d}(\mathbf{r}') \phi_d(\mathbf{r}) |{}_m d^3r d^3r', \quad (2)$$

where  $\phi_d(\mathbf{r})|_m$  is the wave function of the  $3\text{D}^5$  state of the  $\text{Mn}^{2+}$  ion located at the  $m$ th cation layer,  $u_c^{2d}(\mathbf{r})$  is the two-dimensional zone-center Bloch eigenfunction for the  $\Gamma_6$  conduction band, and  $F(z)$  is the normalized envelope function of the quantum well ground state.

Notice that  $\phi_d(\mathbf{r})$  is highly localized at the  $\text{Mn}^{2+}$  ion site of the  $m$ th cation layer (the transfer of the electron density from the  $\text{Mn}^{2+}$  ion to the four nearest anions is less than 1%),<sup>8</sup>  $u_c^{2d}(\mathbf{r})$  oscillates rapidly with the period of the unit cell of the bulk crystal, and the exchange interaction  $V(\mathbf{r} - \mathbf{r}')$  is

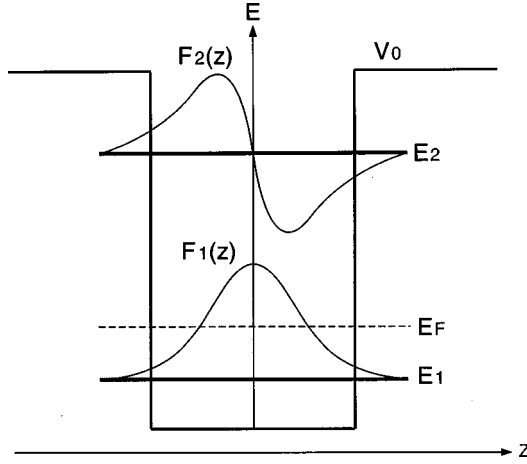


FIG. 1. Schematic diagram of a (001) quantum well showing both energy levels and wave functions of the quantum well states.

only important at (or very near) the  $\text{Mn}^{2+}$  site—i.e., when  $|\mathbf{r}-\mathbf{r}'|$  is small. The dominant contribution to the exchange integral thus comes only from the region of the  $m$ th cation layer. However,  $F(z)$  is basically a constant within the region of the  $m$ th layer [ $F(z)$  is a slowly varying function compared to the width ( $a_L/4$ ) of the  $m$ th atomic layer, where  $a_L$  is the lattice parameter of the semiconductor host]. We can therefore replace  $F(z)$  by its average value at the  $m$ th layer, denoted by  $F(z_m)$ , and we can take it out of the integral.<sup>9</sup> This yields

$$J(m) = -2F^*(z_m)F(z_m) \int \int u_c^{2d*}(\mathbf{r})\phi_d^*(\mathbf{r}') \times V(\mathbf{r}-\mathbf{r}')u_c^{2d}(\mathbf{r}')\phi_d(\mathbf{r})d^3r d^3r'. \quad (3)$$

Equation (1) then acquires the relatively simple, and physically more transparent, form,

$$H_{\text{ex}}(m) = \alpha^{2d}|F(z_m)|^2 \mathbf{S} \cdot \left[ \sum_{\mathbf{k}_{xy}, \gamma} \boldsymbol{\sigma}_{\mathbf{k}_{xy}, \gamma} f(\mathbf{k}_{xy}, T) \right], \quad (4)$$

where we define  $\alpha^{2d}$  as the two-dimensional exchange constant:

$$\alpha^{2d} = -2 \int \int u_c^{2d*}(\mathbf{r})\phi_d^*(\mathbf{r}') \times V(\mathbf{r}-\mathbf{r}')u_c^{2d}(\mathbf{r}')\phi_d(\mathbf{r})d^3r d^3r'. \quad (5)$$

We now derive the EPR line shift for the  $\text{Mn}^{2+}$  ion in the  $m$ th cation layer of the quantum well. The summation in the brackets of Eq. (4) represents the spin polarization of the band electrons. When a magnetic field  $\mathbf{H}$  is applied along the growth direction  $z$ , we can express such spin polarization as  $n_e^{2d}\langle\sigma_z\rangle\hat{\mathbf{z}}$ , where  $n_e^{2d}$  is the two-dimensional electron concentration in the quantum well, and  $\langle\sigma_z\rangle$  is the average spin polarization per electron. The exchange Hamiltonian can now be written as

$$H_{\text{ex}}(m) = \alpha^{2d}|F(\mathbf{z}_m)|^2 n_e^{2d}\langle\sigma_z\rangle S_z, \quad (6)$$

or

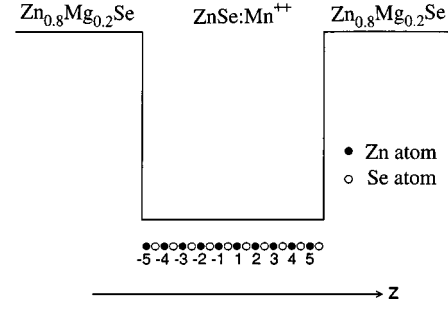


FIG. 2. Schematic diagram of a  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}/\text{ZnSe}/\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}$  quantum well structure. The well region contains ten layers of ZnSe, with a very low concentration of  $\text{Mn}^{2+}$  ions that occupy the Zn sites at random points.

$$H_{\text{ex}}(m) = N_0^{2d} \alpha^{2d} |F(\mathbf{z}_m)|^2 \xi_e^{2d} \langle\sigma_z\rangle S_z, \quad (7)$$

where  $N_0^{2d}$  is the cation density in the  $xy$  atomic plane, and  $\xi_e^{2d} = n_e^{2d}/N_0^{2d}$ . We have shown in the Appendix that  $N_0^{2d} \alpha^{2d} = N_0 \alpha$ , where  $N_0$  is the bulk cation density, and  $\alpha$  is the commonly used three-dimensional exchange integral.<sup>7</sup> We can thus write the exchange Hamiltonian in the compact form

$$H_{\text{ex}}(m) = N_0 \alpha |F(z_m)|^2 \xi_e^{2d} \langle\sigma_z\rangle S_z. \quad (8)$$

Using Eq. (8), we obtain the expression for the shift of the spin level characterized by the magnetic quantum number  $m_s$  of the  $\text{Mn}^{2+}$  ion located in the  $m$ th cation layer of the quantum well,

$$\delta E_{m_s}(m) = N_0 \alpha |F(z_m)|^2 \xi_e^{2d} \langle\sigma_z\rangle m_s. \quad (9)$$

Correspondingly, the change of the magnetic field at which the transition  $m_s \rightarrow m_s - 1$  appears is given by

$$\delta H_{m_s \rightarrow m_s - 1}(m) = N_0 \alpha |F(z_m)|^2 \xi_e^{2d} \langle\sigma_z\rangle / g_{\text{Mn}} \mu_B. \quad (10)$$

As can be readily seen from Eq. (10), the EPR line shift of a  $\text{Mn}^{2+}$  ion located in the  $m$ th cation layer of the quantum well is directly proportional to the square of the amplitude of the envelope function *evaluated at that atomic layer*. Based on this, we propose that  $\text{Mn}^{2+}$  ions can be used as built-in probes for measuring the spatial dependence of the probability density (i.e., the square of the wave function amplitude) associated with the electronic states confined in II-VI semiconductor quantum wells. Let us suppose that the material in the well is ZnSe. The  $\text{Mn}^{2+}$  ions will then be located only in the atomic layers occupied by Zn, i.e., they will be restricted to discrete values of  $z$ . Thus, in a well consisting of  $n_w$  layers of ZnSe (as shown in Fig. 2), there will be  $n_w$  nonequivalent groups of  $\text{Mn}^{2+}$  ions: owing to the variation of the wave function in the  $z$  direction, the  $\text{Mn}^{2+}$  ions located in different Zn layers will experience different EPR line shifts, depending on the wave function amplitude at that layer. This will result in the splitting into  $n_w$  discrete lines of each of the EPR lines. By measuring these EPR shifts, one can get direct information on the electronic wave function distribution along the growth direction in the quantum well.

As an example, we discuss the results of our numerical calculations for the shift of the EPR line of  $\text{Mn}^{2+}$  ions very

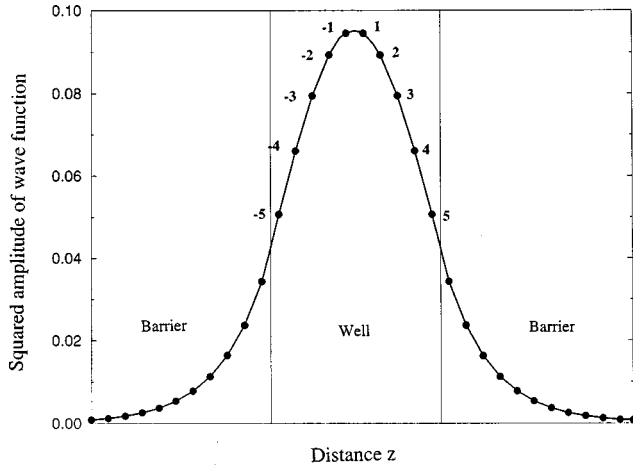


FIG. 3. The square of the electron wave function (solid line), and its average value at each cation layer (dots), calculated by the  $\mathbf{k}\cdot\mathbf{p}$  approximation for the ground state of a  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}/\text{ZnSe}/\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}$  conduction band quantum well.

sparingly distributed in the well region of a  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}/\text{ZnSe}/\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}(001)$  single quantum well. The quantum well structure under consideration is shown in Fig. 2, with ten ZnSe layers in the well region denoted by  $-5, -4, -3, \dots, 4, 5$ . To evaluate the EPR shift, we must first calculate the electronic wave function of the ground state in the well. The energy eigenvalues and wave functions of the states confined in such a quantum well with the magnetic field applied parallel to the growth direction were calculated in the  $\mathbf{k}\cdot\mathbf{p}$  approximation using the finite element method described in Ref. 5. In the present calculation, the energy band parameters and strain parameters for ZnSe were obtained from Ref. 10. To describe the  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}$  barrier, we have chosen the same parameters as those of ZnSe with the exception of the band gap, which is given by  $E_g = 2.82 + 1.28x$ , with  $x = 0.20$ .<sup>11</sup> The valence band offset was taken as 30% of the energy gap difference of ZnSe and  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}$ .<sup>11</sup> The results show that there is only one state confined in the conduction-band quantum well at 72 meV above the bottom of the well. The calculated square of the wave function for the ground state (the solid line), and the values of  $|F(z_m)|^2$  at the cation planes (solid dots) are shown in Fig. 3.

The spin polarization of the conduction band electrons,  $\langle\sigma_z\rangle$ , can be calculated in the following way. When a magnetic field  $\mathbf{H}$  is applied along the growth direction  $z$ , a series of Landau levels will be formed with electron energies given by

$$E_{n,\gamma} = E_1 + (n + \frac{1}{2})\hbar\omega_c + g_e\mu_B\sigma_z(n,\gamma)H, \quad n = 0, 1, 2, \dots, \quad (11)$$

where  $\omega_c = eH/m^*c$ . In this case the spin polarization of the conduction band electrons can be directly evaluated from the following equation:

$$\langle\sigma_z\rangle = \sum_{n,\gamma} \frac{\sigma_z(n,\gamma)}{1 + \exp[(E_{n,\gamma} - E_F)/kT]}. \quad (12)$$

The Fermi level  $E_F$  for a given electron concentration, magnetic field, and temperature is determined by

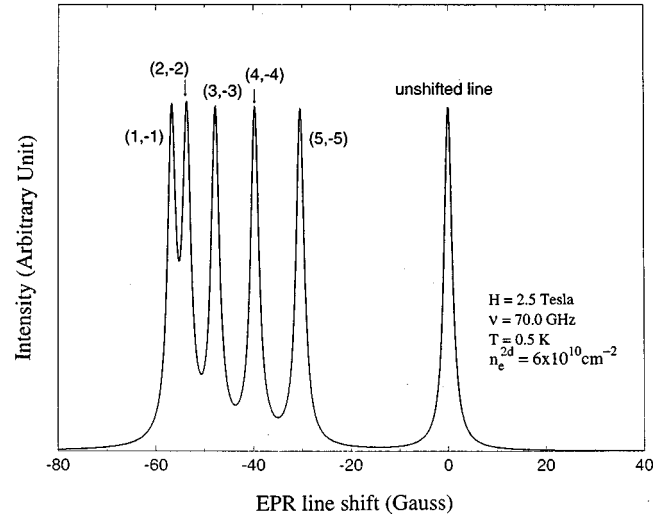


FIG. 4. Calculated EPR line shifts of the  $\text{Mn}^{2+}$  ions in the well region of the  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}/\text{ZnSe}/\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}$  quantum well structure at  $T = 0.5$  K and  $H = 2.5$  T, i.e., corresponding to an EPR experiment performed at 70.0 GHz.

$$\rho \sum_{n,\gamma} \frac{1}{1 + \exp[(E_{n,\gamma} - E_F)/kT]} = n_c^{2d}, \quad (13)$$

where the Landau level energy  $E_{n,\gamma}$  is given by Eq. (11), and  $\rho = eH/hc$  is the orbital degeneracy. Once the Fermi level  $E_F$  is obtained from Eq. (13), the spin polarization of the band electrons can then be calculated from Eq. (12).

To evaluate the EPR line shifts of  $\text{Mn}^{2+}$  ions in the well region of a  $\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}/\text{ZnSe}/\text{Zn}_{0.8}\text{Mg}_{0.2}\text{Se}$  single quantum well, we take the experimentally measured value  $N_0\alpha = 0.26$  eV of Ref. 12 for ZnSe, and assume the two-dimensional electron concentration  $n_e^{2d}$  to be  $6.0 \times 10^{10} \text{ cm}^{-2}$ , a value typical for a moderately doped semiconductor. Using the calculated values of  $|F(z_m)|^2$  from the finite element method, Fig. 4 shows the EPR line shifts obtained from Eq. (10) at a magnetic field  $H = 2.5$  T (70 GHz) and a temperature  $T = 0.5$  K. We show the field shifts of only one of the 30 EPR lines, since the shift patterns are *identical* for all 30 lines. The EPR linewidth is usually very small at low temperatures (typically less than 0.5 G at 4.2 K for dilute  $\text{Mn}^{2+}$  concentrations)<sup>8</sup> and we take it as 1 G in Fig. 4. Due to the reflection symmetry of the quantum well about its center, the  $\text{Mn}^{2+}$  ions in atomic layers equidistant from the center of the well experience the same shifts, given by the lines denoted by  $(m, -m)$  in Fig. 4. The important feature is that  $\text{Mn}^{2+}$  ions located in *different* layers experience *different* line shifts, thus giving a direct measure of the probability density distribution along the growth direction in the well region. It can be seen from Fig. 4 that these EPR line shifts are in the range of 25–50 G, easily measurable by standard EPR techniques. If such shifts are determined by experiment, one then automatically obtains a mapping of the wave function distribution via Eq. (10).

In this connection one should emphasize the inherent sensitivity and precision characteristic of EPR measurements in solids. For example, EPR has much better accuracy than many optical techniques for determining the presence of impurities in a crystal lattice. Its sensitivity is nominally better

than  $10^{10}$  spins,<sup>13</sup> which means that in a typical sample of 10 mm by 2 mm, a relative concentration of  $10^{-4}$  Mn atoms in one monatomic layer should be readily detected. Also, the determination of the EPR position and the EPR resolution are usually extremely precise. Typically, shifts of a few tenths of 1 G can be measured, and this corresponds to an error of about  $10^{-3}$  in the measurement of the square of the wave function amplitude. In fact, EPR has been the only successful technique for mapping the electronic wave function distributions of point defects (deep and shallow levels) in semiconductors.<sup>13,14</sup>

In summary, we have investigated the effect of exchange interaction between the localized  $d$  electrons of a  $\text{Mn}^{2+}$  ion and semiconductor band electrons on the Zeeman transitions of  $\text{Mn}^{2+}$  ions located in II-VI semiconductor quantum wells. We have shown that such exchange-interaction-induced line shift of  $\text{Mn}^{2+}$  EPR is directly proportional to the local electron probability density that the  $\text{Mn}^{2+}$  ion ‘‘sees’’ at its specific site in the well. This suggests that  $\text{Mn}^{2+}$  ions can be used as built-in localized probes for mapping the spatial probability distribution (i.e., wave function amplitude) of electronic states confined in II-VI semiconductor quantum wells.

The authors thank M. Dobrowolska and J. Kossut for illuminating discussions. The use of the Finite Element Method programs made available at Quantum Algorithms, Inc. by L. R. Ram-Mohan is gratefully acknowledged. This work was supported by NSF Grant No. DMR97-05064.

#### APPENDIX: THE EXCHANGE CONSTANTS $N\alpha$ AND $N^{2d}\alpha^{2d}$

In this appendix we show that  $N\alpha = N^{2d}\alpha^{2d}$ . By definition, the two-dimensional exchange integral is [see Eq. (5)]

$$\alpha^{2d} = -2 \int \int u_c^{2d*}(\mathbf{r}) \phi_d^*(\mathbf{r}') \times V(\mathbf{r}-\mathbf{r}') u_c^{2d}(\mathbf{r}') \phi_d(\mathbf{r}) d^3r d^3r', \quad (\text{A1})$$

where  $u_c(\mathbf{r})$  is the two-dimensional zone-center Bloch function of the conduction band, which can be formed in terms of the Bloch summation of the atomic  $s$ -orbital  $\psi_s$  in the  $x$ - $y$  atomic plane under consideration (say, the  $m$ th cation layer):<sup>15</sup>

$$u_c^{2d}(\mathbf{r}) = \frac{1}{\sqrt{N^{2d}}} \sum_{\mathbf{R}_i} \psi_s(\mathbf{r}-\mathbf{R}_i). \quad (\text{A2})$$

The summation over  $\mathbf{R}_i$  is limited to the atomic plane in question. Substituting Eq. (A2) into Eq. (A1), we have

$$N^{2d}\alpha^{2d} = -2 \sum_{\mathbf{R}_i} \sum_{\mathbf{R}_j} \int \int \psi_s^*(\mathbf{r}-\mathbf{R}_i) \phi_d^*(\mathbf{r}'-\mathbf{R}_j) V[(\mathbf{r}-\mathbf{R}_i) - (\mathbf{r}'-\mathbf{R}_j)] \psi_s(\mathbf{r}-\mathbf{R}_j) \phi_d(\mathbf{r}-\mathbf{R}_i) d^3r d^3r'. \quad (\text{A3})$$

Suppose now that the magnetic ion occupies the site  $\mathbf{R}_0$ . Since the  $3d$  electrons are basically localized at the magnetic ion site and the exchange potential  $V$  is only important at (or very near) that magnetic ion site, the contributions to the integral  $\alpha$  from terms  $\mathbf{R}_i, \mathbf{R}_j \neq \mathbf{R}_0$  are small, and can be neglected. Equation (A3) then becomes

$$N^{2d}\alpha^{2d} = -2 \int \int \psi_s^*(\mathbf{r}-\mathbf{R}_0) \phi_d^*(\mathbf{r}'-\mathbf{R}_0) V(\mathbf{r}-\mathbf{r}') \times \psi_s(\mathbf{r}'-\mathbf{R}_0) \phi_d(\mathbf{r}-\mathbf{R}_0) d^3r d^3r'. \quad (\text{A4})$$

If we take  $\mathbf{R}_0$  as the origin of the coordinate system, one can write Eq. (A4) as

$$N^{2d}\alpha^{2d} = -2 \int \int \psi_s^*(\mathbf{r}) \phi_d^*(\mathbf{r}') V(\mathbf{r}-\mathbf{r}') \times \psi_s(\mathbf{r}') \phi_d(\mathbf{r}) d^3r d^3r'. \quad (\text{A5})$$

Comparing Eq. (A6) in the Appendix of Ref. 7 with Eq. (A5) above, we then have

$$N^{2d}\alpha^{2d} = N\alpha. \quad (\text{A6})$$

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