

Perturbation theory of exchange interaction

C. J. Chen* and R. Wiesendanger

Institute of Applied Physics and Microstructure Research Center, University of Hamburg, Jungiusstrasse 11, 20355 Hamburg, Germany

(Received 19 July 2006; published 5 September 2006)

Exchange interaction is the conceptual foundation to the understanding of the covalent bond, ferromagnetism, and electron transport phenomenon. However, its evaluation has always been a formidable problem. We show that within the Hartree-Fock and muffin-tin potential approximations, using time-dependent perturbation theory, simple analytic expressions of the exchange interaction between two atomic states can be obtained. To assess the accuracy of the method, we evaluated the dissociation energies and the vibrational frequencies for homonuclear diatomic molecules built from atoms in the first two rows of the periodic table. The theoretical predictions agree well with experimental values and the accuracy matches that of typical first-principle computations.

DOI: [10.1103/PhysRevB.74.113102](https://doi.org/10.1103/PhysRevB.74.113102)

PACS number(s): 71.70.Gm, 31.15.Md, 31.15.Rh, 34.20.Cf

Since the seminal work of Heitler and London,¹ exchange interaction has been the conceptual foundation of the covalent bond^{2,3} and ferromagnetism.⁴ In nanoscience and nanotechnology, the understanding of atomic forces,⁵⁻¹⁰ magnetic nanostructures,¹¹ and electron transport¹² also relies on the concept of exchange interaction. However, the evaluation of the exchange integral^{3,13} has always been a formidable problem.^{14,15}

As pointed out by Herring,¹⁶ the Heitler-London method¹ predicts a wrong sign of the exchange interaction at large internuclear distances, besides a 33% error in the dissociation energy. In 1962, Herring¹⁶ and Landau¹⁷ independently developed a perturbation method, resulting in a surface-integral expression for the exchange interactions. For the hydrogen molecule, an exact asymptotic expression is derived.^{18,19} That method was applied to the asymptotic behavior of diatomic molecules with alkali metal atoms.²⁰ Using an interpolating method, the exchange interaction for the entire distance range can be obtained.²¹ However, those methods¹⁸⁻²¹ can only apply to hydrogen-like atoms.

Here we show that within the Hartree-Fock and the muffin-tin potential approximations,²² their method can be extended to general diatomic molecules over intermediate internuclear distances. Using time-dependent perturbation theory, we show that the expression of exchange interaction as a surface integral^{16,17} is mathematically identical to the tunneling matrix elements of Bardeen.²³ Using the derivative rule,⁵ the surface integral can be reduced to simple analytic expressions. The constants therein can be evaluated from the Roothaan-Hartree-Fock atomic wave functions.^{24,25} By introducing an equilibrium internuclear distance, using the Morse function,^{3,26} potential energy curves on the entire distance range are obtained.

To assess the accuracy of the method, we derived dissociation energies and vibrational frequencies for homonuclear diatomic molecules from atoms of the first two rows of the periodic table. The results are in good agreement with experimental data^{26,27} and its accuracy matches that of typical first-principle computations.^{28,29}

For the purpose of computing dissociation energies at equilibrium configurations, first-principle numerical methods, especially the density-functional theory, are more general and powerful.^{28,29} The analytic approach, on the other

hand, may provide deeper understanding of the underlying physics, for example, by deriving analytic expressions for systematic behaviors and correlations.

The muffin-tin potential approximation is well tested in the band-structure computation of solids.²² An implementation to homonuclear diatomic molecules is shown in Fig. 1. For each atom, within a radius r_m , the potential is spherically symmetric. Outside r_m , the potential equals the vacuum level, $U=0$. The single-electron Schrödinger's equations of free atoms are

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + U_A \right] \psi_{A,nlm} = E_{nl} \psi_{A,nlm}, \quad (1)$$

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + U_B \right] \psi_{B,nlm} = E_{nl} \psi_{B,nlm}, \quad (2)$$

where n is the principal quantum number, l is the azimuthal quantum number, and m is the magnetic quantum number. After the two atoms approach each other to form a molecule, the time-dependent Schrödinger's equation of an electron is

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \equiv \left[-\frac{\hbar^2}{2m_e} \nabla^2 + U_A + U_B \right] \Psi. \quad (3)$$

Similar to Bardeen's tunneling theory,²³ we assume that the unperturbed atomic wave functions of the two atoms are almost orthogonal,

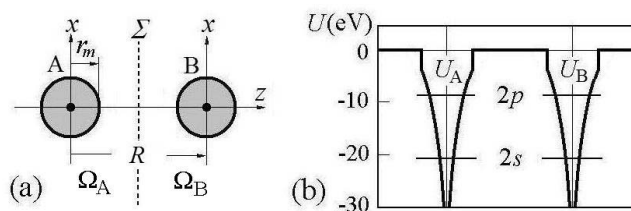


FIG. 1. Muffin-tin potential for a homonuclear diatomic molecule. Inside the muffin-tin radius r_m , the potential is spherically symmetric. Outside r_m , the potential equals the vacuum level, $U=0$. Schematically, the energy levels for $2s$ and $2p$ electrons of carbon are shown.

$$\int \psi_{A,nlm}^* \psi_{B,n'l'm'} d\tau \cong 0. \quad (4)$$

The symmetry of the problem suggests the ansatz,

$$\Psi = c_A(t) \psi_{A,nlm} e^{-E_{nl}t/\hbar} + c_B(t) \psi_{B,nlm} e^{-E_{nl}t/\hbar}, \quad (5)$$

where $c_A(t)$ and $c_B(t)$ are time-dependent coefficients to be determined by Eq. (3). Intuitively, the two wave functions in Eq. (5) should have the same n , l , and m . This point will be verified later. For clarity, from now on, the labels nlm are omitted. Using Eq. (3), noticing that inside muffin tin A, the amplitude of the wave function of atom B is negligible, and vice versa,

$$\int \psi_A^* U_B \psi_A d\tau \cong \int \psi_B^* U_A \psi_B d\tau \cong 0, \quad (6)$$

we obtain the following equations for the coefficients,

$$\begin{aligned} i\hbar \dot{c}_A(t) &= M_B c_B(t), \\ i\hbar \dot{c}_B(t) &= M_A c_A(t), \end{aligned} \quad (7)$$

where

$$M_A = \int \psi_B^* U_A \psi_A d\tau, \quad (8)$$

$$M_B = \int \psi_A^* U_B \psi_B d\tau. \quad (9)$$

Because U_A is nonzero only in the muffin tin of atom A, Eq. (8) can be evaluated over a volume Ω_A containing muffin tin A but not muffin tin B. The simplest choice is to use the median plane Σ as the boundary, see Fig. 1. Using Eq. (1), Eq. (8) becomes

$$M_A = \int_{\Omega_A} \psi_B^* \left[E_{nl} + \frac{\hbar^2}{2m_e} \nabla^2 \right] \psi_A d\tau. \quad (10)$$

Using Eq. (2) and notice that in Ω_A , $U_B=0$, we have

$$M_A = \frac{\hbar^2}{2m_e} \int_{\Omega_A} [\psi_B^* \nabla^2 \psi_A - \psi_A \nabla^2 \psi_B^*] d\tau. \quad (11)$$

Using Green's theorem, the volume integral can be converted into a surface integral on Σ ,

$$M_A = \frac{\hbar^2}{2m_e} \int_{\Sigma} [\psi_B^* \nabla \psi_A - \psi_A \nabla \psi_B^*] \cdot d\mathbf{S}. \quad (12)$$

Mathematically, it is identical to Bardeen's tunneling matrix element.²³ Similarly, M_B can also be converted into a surface integral. By adjusting the relative phase of ψ_A and ψ_B , both M_A and M_B can be made real and non-negative. Denoting

$$M = M_B = M_A, \quad (13)$$

we obtain two independent solutions of Eq. (3),

TABLE I. Numerical coefficients in Eq. (20).

l	$ m $	Bond type	a_1	a_2	a_3	a_4	a_5
0	0	$s\sigma, s\sigma^*$	1	0	0	0	0
1	0	$p\sigma, p\sigma^*$	3	6	6	0	0
1	1	$p\pi, p\pi^*$	0	3	3	0	0
2	0	$d\sigma, d\sigma^*$	5	25	85	180	180
2	1	$d\pi, d\pi^*$	0	15	75	180	180
2	2	$d\delta, d\delta^*$	0	0	60	180	180

$$\Psi_1 = [\cos(Mt/\hbar) \psi_A + i \sin(Mt/\hbar) \psi_B] e^{-iE_{nl}t/\hbar}, \quad (14)$$

and

$$\Psi_2 = [\cos(Mt/\hbar) \psi_B + i \sin(Mt/\hbar) \psi_A] e^{-iE_{nl}t/\hbar}. \quad (15)$$

Two stationary-state solutions can be obtained as linear combinations of Eqs. (14) and (15),

$$\Psi_e = \frac{\Psi_1 + \Psi_2}{\sqrt{2}} = \frac{\psi_A + \psi_B}{\sqrt{2}} e^{-i(E_{nl}-M)t/\hbar}, \quad (16)$$

$$\Psi_o = \frac{\Psi_1 - \Psi_2}{\sqrt{2}} = \frac{\psi_A - \psi_B}{\sqrt{2}} e^{-i(E_{nl}+M)t/\hbar}. \quad (17)$$

Here, Ψ_e is the even, or bonding molecular orbital, with a lower energy eigenvalue; and Ψ_o is the odd, or antibonding molecular orbital, with a higher energy eigenvalue. The covalent-bond energy $E_c(R)$, as a function of the internuclear distance R , is

$$E_c(R) = \mp M. \quad (18)$$

The surface integral in Eq. (12) can be evaluated using the derivative rule in tunneling theory.⁵ Outside the muffin tin, the atomic wave function is

$$\psi_{nlm} = C_{nl} k_l(\kappa r) Y_{lm}(\theta, \varphi), \quad (19)$$

where r is the electron-nucleus distance, $k_l(\rho)$ is a modified spherical Bessel function, Y_{lm} is spherical harmonics. For the constants κ and C_{nl} , see below. The general result is

$$E_c(R) = \mp M = \mp \frac{1}{2} \frac{C_{nl}^2 \hbar^2}{\kappa m_e} e^{-\kappa R} \sum_n \frac{a_n}{(\kappa R)^n}. \quad (20)$$

The numerical coefficients a_n are listed in Table I.

The constants κ and C_{nl} in Eqs. (19) and (20) can be obtained from the Roothaan-Hartree-Fock atomic wave functions.^{24,25} The constant κ is related to the energy level of the atomic state,

$$\kappa = \sqrt{-2m_e E_{nl}}/\hbar. \quad (21)$$

The constant C_{nl} is obtained by a least-squares fit to the Roothaan-Hartree-Fock radial atomic wave functions $R_{nl}(r)$ for $r > r_m$:

TABLE II. Experimental and theoretical data for homonuclear diatomic molecules. Column 1 is the molecule. Column 2 is the ground state of the free atom. Column 3 is the ground state of the molecule, see Ref. 26. Contents of columns 4, 5, 8, 11, and 13 are taken from Ref. 27. Column 5, R_e , is the experimental equilibrium internuclear distance. Column 6, E_{nl} , is the orbital energy of the outermost valence electron, taken from Refs. 24 and 25. Column 7 is the constant κ , computed from the orbital energy using Eq. (21). Column 8, μ is the reduced mass of the molecule. Column 9, C_{nl} , is the normalization constant of the atomic wave function outside the muffin tin, obtained through a least-squares fit with the Roothaan-Hartree-Fock atomic wave functions. Column 10, a , is the constant in the Morse curve, obtained through a least-squares fit using Eq. (24). Column 11, D_{exp} , is the experimental dissociation energy. Column 12, D_{theo} , is the theoretical dissociation energy, obtained from the parameter of the Morse curve. Column 13, ω_{exp} , is the experimental vibrational frequency. Column 14, ω_{theo} , is the theoretical vibrational frequency, obtained through Eq. (25).

Mol.	AtSt	MolSt	Lowest electron configuration	R_e (Å)	E_{nl} (eV)	κ (Å ⁻¹)	μ (amu)	C_{nl} (Å ^{3/2})	a (Å ⁻¹)	D_{exp} (eV)	D_{theo} (eV)	ω_{exp} (cm ⁻¹)	ω_{theo} (cm ⁻¹)
Li ₂	² S _{1/2}	¹ Σ _g ⁺	KK(2sσ) ²	2.67	5.30	1.18	3.51	2.23	1.48	1.04	1.19	351	662
B ₂	² P _{1/2}	³ Σ _g ⁻	KK(2sσ) ² (2sσ*) ² (2pπ) ²	1.59	8.43	1.49	5.50	2.26	2.31	3.00	3.35	1051	1260
C ₂	³ P ₀	¹ Σ _g ⁺	KK(2sσ) ² (2sσ*) ² (2pσ) ² (2pπ) ²	1.23	11.79	1.76	6.00	2.62	2.82	6.21	5.45	1961	1884
N ₂	⁴ S _{3/2}	¹ Σ _g ⁺	KK(2sσ) ² (2sσ*) ² (2pσ) ² (2pπ) ⁴	1.09	15.44	2.01	7.00	3.98	3.19	9.76	10.49	2358	2725
O ₂	³ P ₂	³ Σ _g ⁻	KK(2sσ) ² (2sσ*) ² (2pσ) ² (2pπ) ⁴ (2pπ*) ²	1.21	17.19	2.12	8.00	3.29	3.25	5.12	3.58	1580	1470
F ₂	² P _{3/2}	¹ Σ _g ⁺	KK(2sσ) ² (2sσ*) ² (2pσ) ² (2pπ) ⁴ (2pπ*) ⁴	1.41	19.86	2.28	9.50	5.23	3.14	1.60	3.09	916	1247
Na ₂	² S _{1/2}	¹ Σ _g ⁺	KKLL(3sσ) ²	3.08	4.77	1.14	11.50	4.45	1.54	0.72	2.90	159	541
Al ₂	² P _{1/2}	³ Σ _g ⁻	KKLL(3sσ) ² (3sσ*) ² (3pπ) ²	2.46	5.71	1.22	11.99	2.41	1.73	1.50	1.69	350	456
Si ₂	³ P ₀	³ Σ _g ⁻	KKLL(3sσ) ² (3sσ*) ² (3pσ) ² (3pπ) ²	2.25	8.08	1.46	13.49	3.79	2.00	3.21	2.27	511	568
P ₂	⁴ S _{3/2}	¹ Σ _g ⁺	KKLL(3sσ) ² (3sσ*) ² (3pσ) ² (3pπ) ⁴	1.89	10.65	1.67	15.49	4.44	2.33	5.03	3.32	780	753
S ₂	³ P ₂	³ Σ _g ⁻	KKLL(3sσ) ² (3sσ*) ² (3pσ) ² (3pπ) ⁴ (3pπ*) ²	1.89	11.9	1.77	15.98	5.40	2.42	2.46	3.51	726	795
Cl ₂	² P _{3/2}	¹ Σ _g ⁺	KKLL(3sσ) ² (3sσ*) ² (3pσ) ² (3pπ) ⁴ (3pπ*) ⁴	1.99	13.78	1.90	17.48	7.24	2.50	2.48	3.16	559	742

$$\int_{r_m}^{\infty} [C_{nl}k_l(\kappa r) - R_{nl}(r)]^2 dr = \min. \quad (22)$$

In the established practice of the APW method,²² the muffin-tin radius is defined as equal or slightly smaller than one half of the equilibrium internuclear distance. Here we take $r_m=0.4R_e$. The results for 12 elements are listed in Table II. Typical distance dependence of the interaction energies is shown in Fig. 2.

Using the *Aufbau* process,^{3,17,26} the total covalent-bond interaction energy $E_c(R)$ can be obtained. For inert-gas atoms, He, Ne, and Ar, and alkali-earth metals, Be and Mg, the bonding and antibonding interactions are paired. The total covalent bond interaction energy is zero. For other molecules, see Table II.

To construct the potential curve on the entire distance range, we use the Morse function^{3,26}

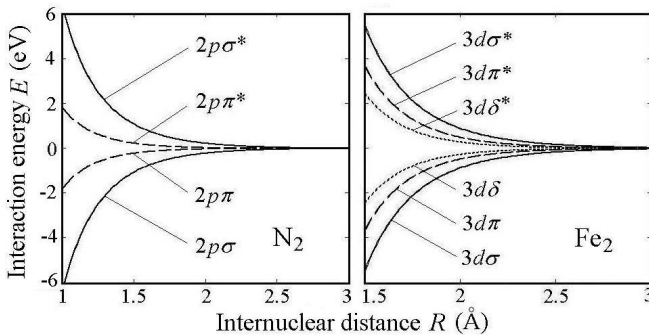


FIG. 2. Distance dependence of exchange interaction energy. The examples of N₂ and Fe₂ are shown.

$$E(R) = D_e [e^{-2a(R-R_e)} - 2e^{-a(R-R_e)}], \quad (23)$$

where D_e is the dissociation energy, and a is a constant. The equilibrium internuclear distance R_e is introduced as an empirical parameter. Parameters D_e and a can be determined by fitting the attractive component of the Morse function with the covalent-bond interaction energy $E_c(R)$ down to R_e ,

$$\int_{R_e}^{\infty} [2D_e e^{-a(R-R_e)} - E_c(R)]^2 dR = \min. \quad (24)$$

The dissociation energies thus predicted are listed in Table II and Fig. 3.

The vibrational frequency of the ground state molecule, ω_e , can be obtained from the constants in the Morse function through the relation^{3,26}

$$\omega_e = \frac{a}{2\pi c} \sqrt{\frac{2D_e}{\mu}} \cong 698a \sqrt{\frac{D_e}{\mu}}, \quad (25)$$

where c is the speed of light, and μ is the reduced mass of the molecule, in atomic unit, $m(^{12}\text{C})/12$. A comparison of theoretical data with experimental data²⁷ is also shown in Table II and Fig. 3. As shown, besides alkali metals (especially Na, where the muffin-tin potential fails because of the huge orbital radius), the theoretical values agree well with experimental values. The accuracy is in line with the accuracy of typical first-principle computations using the local-density approximation, 10–20 % in dissociation energy.²⁹

Although we exemplified the method with homonuclear diatomic molecules, it can easily be applied to heteronuclear cases. The theory only requires that the energy levels of the relevant states are aligned. For example, in Fe₃O₄, the partial

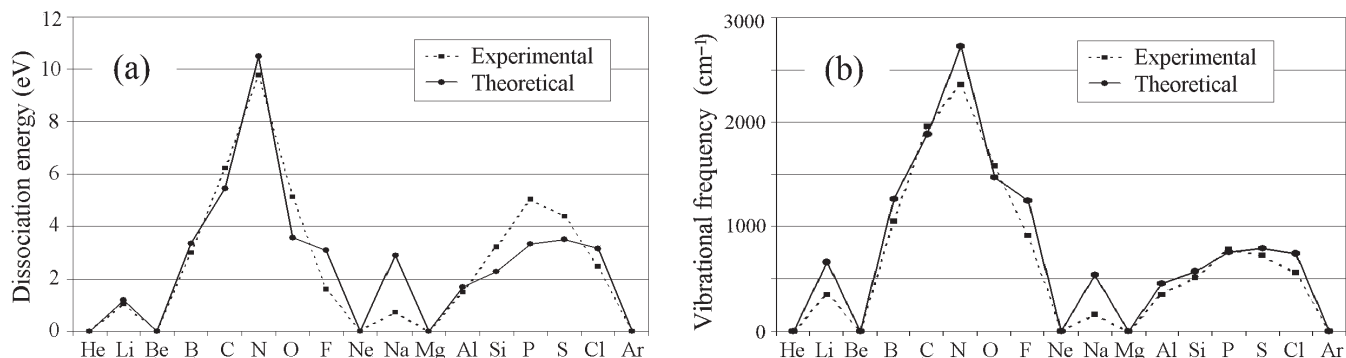


FIG. 3. Comparison between experimental and theoretical data for homonuclear diatomic molecules, see Table II. (a) dissociation energy. (b) vibrational frequency. The experimental data are taken from Ref. 27. As shown, besides alkali metals, such as Na, the theoretical predictions agree reasonably well with experimental values.

ionic bonding of Fe-O makes the energy levels aligned. The derivative rule works for any combination of electron wavefunctions if one of them is in the form of Eq. (19).

In conclusion, we have derived simple analytic expressions of the exchange interaction within the Hartree-Fock and muffin-tin potential approximations. The dissociation energies and the vibrational frequencies thus predicted agree well with experimental values. The accuracy matches that of typical first-principle numerical computations. The method

can be applied to problems in nanoscience and nanotechnology, including atomic forces, nanomagnetism, and electron transfer in molecules.

This work is supported by the Deutsche Forschungsgemeinschaft (SFB 668). The authors wish to thank Stefan Heinze, Elena Vedmedenko, Oswald Pietzsch, Andrea Kubetzka, and Yuriy Mokrousov, for inspiring discussions and comments.

*Corresponding author. Email address: jchen@physnet.uni-hamburg.de

- ¹W. Heitler and F. London, *Z. Phys.* **44**, 455 (1927).
- ²L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960).
- ³C. A. Coulson, *Valence* (Oxford University Press, London, 1969).
- ⁴W. Heisenberg, *Z. Phys.* **49**, 619 (1928).
- ⁵C. J. Chen, *Introduction to Scanning Tunneling Microscopy* (Oxford University Press, New York, 1993).
- ⁶R. Perez, M. C. Payne, I. Stich, and K. Terakura, *Phys. Rev. Lett.* **78**, 678 (1997).
- ⁷C. Loppacher, M. Bammerlin, M. Guggisberg, S. Schär, R. Bennewitz, A. Baratoff, E. Meyer, and H.-J. Güntherodt, *Phys. Rev. B* **62**, 16944 (2000).
- ⁸T. Arai and M. Tomitori, *Phys. Rev. Lett.* **93**, 256101 (2004).
- ⁹C. J. Chen, *Nanotechnology* **16**, S27 (2005).
- ¹⁰C. J. Chen, *Nanotechnology* **17**, S195 (2006).
- ¹¹E. Y. Vedmedenko, A. Kubetzka, K. von Bergmann, O. Pietzsch, M. Bode, J. Kirschner, H. P. Oepen, and R. Wiesendanger, *Phys. Rev. Lett.* **92**, 077207 (2004).
- ¹²A. Nitzan, *Annu. Rev. Phys. Chem.* **52**, 681 (2001).
- ¹³L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935).
- ¹⁴J. C. Slater, *Rev. Mod. Phys.* **25**, 199 (1953).
- ¹⁵R. Stuart and W. Marshall, *Phys. Rev.* **120**, 353 (1960).

- ¹⁶C. Herring, *Rev. Mod. Phys.* **34**, 631 (1962).
- ¹⁷L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (non-relativistic theory)* (McGraw-Hill, New York, 1977).
- ¹⁸C. Herring and M. Flicker, *Phys. Rev.* **134**, A362 (1964).
- ¹⁹L. P. Gor'kov and L. P. Pitaevskii, *Sov. Phys. Dokl.* **8**, 788 (1964).
- ²⁰S. J. Umanski and A. I. Voronin, *Theor. Chim. Acta* **12**, 166 (1968).
- ²¹I. V. Ponomarev, V. V. Flambaum, and A. L. Efros, *Phys. Rev. B* **60**, 5485 (1999).
- ²²T. Loucks, *Augmented Plane Wave Method* (W.A. Benjamin, Inc., New York, 1967).
- ²³J. Bardeen, *Phys. Rev. Lett.* **6**, 57 (1961).
- ²⁴C. F. Bunge, J. A. Barrientos, and A. V. Bunge, *At. Data Nucl. Data Tables* **53**, 113 (1993).
- ²⁵The above Roothaan-Hartree-Fock atomic wave functions are available at www.ccl.net/cca/data/atomic-RHF-wavefunctions/tables in computer-readable format.
- ²⁶G. Herzberg, *Spectra of Diatomic Molecules* (D. van Nostrand, Toronto, 1950).
- ²⁷K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (D. van Nostrand, Toronto, 1979).
- ²⁸J. A. Pople, Nobel Lecture: Quantum Chemical Models (1998).
- ²⁹W. Kohn, Nobel Lecture: Electronic Structure of Matter—Wavefunctions and Density Functionals (1999).