Two-center magnetic-multipole interaction between atoms, molecules, and nuclei

Ying-Nan Chiu

Center for Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, D.C. 20064

(Received 28 February 1979)

A general formula in the form of a product of irreducible tensors is derived for the magnetic multipole-multipole interaction of any order between two nonoverlapping charge distributions. These two charge centers may be separate atoms, molecules, or nuclei. In the limit of low order, the formula is shown to reduce to the conventional spin-spin (magnetic dipole-dipole) interaction. It also reduces to a two-center expansion term obtainable from the conventional spin-other-orbit interaction.

Although two-center expansion of electrostatic interaction has been well known,[1-13] two-center expansion of magnetic interaction beyond the dipolar case has been scarce in literature, due in part possibly to mathematical complexity. One exception is the prolate-spheroidal expansions of the spin-orbit, spin-spin, and orbit-orbit operation by Matcha, Pritchard, and Kern.[14] Such expansions are used mainly for the evaluation of molecular integrals[15] in a diatomic molecule and are not expressed in terms of the usual magnetic-multipole moments similar to those of multiple radiation fields.[15-20] Such multipole moments in tensorial form are needed for the study of angular-momentum coupling and other symmetry properties of the interaction. The magnetic-multipole interaction for hyperfine structure such as that derived by Schwartz[21] and later by others[19] is a one-center expansion applicable to the interaction of the atomic electron with the same atom's nuclear electric and magnetic moments.[22] The present work is to derive the two-center magnetic-multipole interaction of any order in irreducible tensorial form. It can be used for example in the mixed higher electric- and magnetic-multipole dispersion interaction[23-25] between two (sometimes optically active) molecular radicals with nonvanishing spin (S) and orbital (L) angular momentum. It will also lead to the formula for nuclear octopole-octopole interaction[25] between two neighboring nuclei (for example,[26-28] in Br^{79}, Br^{81} and In^{115}, I^{127}, etc.).

We start by considering two electrons (or spins) i and j at two widely separated centers with i closely centered around center a and j around center b. The extensions of the charges $\vec{r}_i$ and $\vec{r}_j$ are small compared with the separation of centers $\vec{R}$. The generalized current density[19,21] of electron j at center b is

$$\vec{J}_j = -(ie\hbar/mc) g_L \vec{\nabla}_j + (e\hbar/2mc) g_S \vec{\nabla}_j \times \vec{S}_j , \tag{1}$$

This is allowed to interact with the vector potential on j due to the magnetic-multipole moments of i centered on $\vec{a}$[19,21]:

$$\vec{A}_{ij} = \sum_{LM} \frac{i}{L} [\mathfrak{M}^*_{LM}(i) + \mathfrak{M}'^*_{LM}(i)] \times \vec{L}_j [r_{aj}^{-(L+1)} C_{LM}(\theta_{aj}\phi_{aj})] , \tag{2}$$

where $(r_{aj}\theta_{aj}\varphi_{aj})$ are the coordinates of j with respect to the distant center $\vec{a}$ and $C_{LM} = (4\pi/2L+1)^{1/2} Y_{LM}$ is a reduced spherical harmonic. The magnetic 2^L-pole moments are defined in Refs. 19 and 20; i.e., orbital magnetic 2^L pole

$$\mathfrak{M}_{LM}(i) = \frac{1}{L+1} \int \frac{e\hbar}{mc} g_L \vec{\nabla}_i \times [r_i^L C_{LM}(\theta_i \varphi_i)] \cdot \vec{L}_i \, d\vec{r}_i , \tag{3a}$$

and spin-magnetic 2^L pole

$$\mathfrak{M}'_{LM}(i) = \int \frac{e\hbar}{2mc} g_s \vec{\nabla}_i \times [r_i^L C_{LM}(\theta_i \varphi_i)] \cdot \vec{S}_i \, d\vec{r}_i , \tag{3b}$$

where $r_i \theta_i \varphi_i$ refer to the proximal center a. The interaction energy $W = \int \vec{J}_j \cdot \vec{A}_{ij} \, d\vec{r}_j$ may be rearranged to the following by use of the relationships[19]:

$$\vec{L}(r^{-(L+1)} C_{LM}) \cdot \vec{\nabla} = -\vec{\nabla}(r^{-(L+1)} C_{LM}) \cdot \vec{L}$$

and

$$\vec{\nabla} \times \vec{S} \cdot \vec{L} = -\vec{S} \times \vec{\nabla} \cdot \vec{L} = -\vec{S} \cdot \vec{\nabla} \times \vec{L} ,$$

$$W = -\int \frac{e\hbar}{mc} g_L \sum_{LM} \frac{1}{L} \vec{\nabla}_j [r_{aj}^{-(L+1)} C_{LM}(\theta_{aj}\varphi_{aj})] \cdot \vec{L}_j [\mathfrak{M}^*_{LM}(i) + \mathfrak{M}'^*_{LM}(i)] \, d\vec{r}_j + \int \frac{e\hbar}{2mc} g_s \sum_{LM} \frac{i}{L} \vec{S}_j \cdot \vec{\nabla}_j \times \vec{L}_j [r_{aj}^{-(L+1)} C_{LM}(\theta_{aj}\varphi_{aj})] \cdot [\mathfrak{M}^*_{LM}(i) + \mathfrak{M}'^*_{LM}(i)] \, d\vec{r}_j . \tag{4}$$

It is noted here although $\vec{L}$ changes with the translation of center,[29] a scalar product such as $\vec{\nabla}\cdot\vec{L}$ is invariant with respect to translation. Next, we make a translation (from center a to center b) expansion[7] of the reduced spherical harmonics as follows:

$$r_{aj}^{-(L+1)}C_{LM}(\theta_{aj}\varphi_{aj})=\sum_{l}\sum_{M'}(-)^{l+M'}\left(\frac{(2L+2l)!}{(2L)!\,(2l)!}\right)^{1/2}\frac{C(l,L,l+L;M',-M,M'-M)r_i^l C_{lM'}(\theta_j\varphi_j)C_{l+L,M-M'}(\theta\varphi)}{R^{(L+l+1)}}\,, \tag{5}$$

where R is the separation between the two centers a and b and θ, φ are the angular coordinates of vector $\vec{R}$. $r_j\theta_j\varphi_j$ now refer to the proximal center b, with a parallel (to a) set of local coordinates. Substituting of this expansion into Eq. (4), making use of[19] $\vec{\nabla}\times\vec{L}(r^l C_{lM'})=i(l+1)\vec{\nabla}(r^l C_{lM'})$ and neglecting the δ-function singularity for contact interaction, we arrive at

$$W=-\frac{e\hbar}{mc}\int\sum_{LM}\vec{\nabla}_j\Bigg[\sum_{lM'}(-)^{l+M'}\left(\frac{(2L+2l)!}{(2L)!\,(2l)!}\right)^{1/2}\frac{C(l,L,l+L;M',-M,M'-M)r_j C_{lM'}(\theta_j\varphi_j)C_{l+L,M-M'}(\theta\varphi)}{R^{(l+L+1)}}\Bigg]$$
$$\times\left(\frac{g_L\vec{L}_j}{L}+\frac{g_s\vec{S}_j}{2L}(l+1)\right)[\mathfrak{M}^*_{LM}(i)+\mathfrak{M}'^*_{LM}(i)]\,d\vec{r}_j\,. \tag{6}$$

Introducing the definition of magnetic-multipole moments of Eq. (3), and symmetrizing the system with respect to i and j by introducing $\vec{J}_i$ and $\vec{A}_{ji}$ similar to Eqs. (1) and (2), we get

$$W=\tfrac{1}{2}\int(\vec{J}_j\cdot\vec{A}_{ij}\,d\vec{r}_j+\vec{J}_i\cdot\vec{A}_{ji}\,d\vec{r}_i)=-\tfrac{1}{2}\sum_{LM}\sum_{lM'}(-)^{M'}\frac{l+1}{2L}\left(\frac{(2L+2l)!}{(2L)!\,(2l)!}\right)^{1/2}C(l,L,l+L;M',-M,M'-M)$$
$$\times\frac{(-)^l[\mathfrak{M}_{lM'}(j)+\mathfrak{M}'_{lM'}(j)][\mathfrak{M}^*_{LM}(i)+\mathfrak{M}'^*_{LM}(i)]+(-)^L[\mathfrak{M}_{lM'}(i)+\mathfrak{M}'_{lM'}(i)][\mathfrak{M}^*_{LM}(j)+\mathfrak{M}'^*_{LM}(j)]C_{l+L,M-M'}(\theta,\varphi)}{R^{(l+L+1)}}\,, \tag{7}$$

where use is made of the parity of $\mathfrak{M}_{LM}$ under inversion, $(-)^{L-1}$ and the parity of $C_{l+L,M-M'}$, $(-)^{l+L}$. It is also noted[30] that $\mathfrak{M}^*_{LM}=(-)^{1+M}\mathfrak{M}_{L-M}$. An extra factor of $\frac{1}{2}$ is introduced for redundancy of interaction.

Equation (7) is the most general magnetic multipole-multipole interaction of any order for nonoverlapping charges. It has a form similar to the electrostatic multipole-multipole interaction.[31] In the limit of lower order, it reduces to known interactions as follows. For nuclear spin (I) magnetic dipole-dipole interaction, $l=L=1$, Eq. (7) reduces to the known[22,32-34] formula (for *point* magnetic-dipole interaction)

$$W_{\text{s.s.}}=H_{\text{s.s.}}=-6^{1/2}\sum_{MM'}(-)^{M'+M}\frac{C(112;M',-M,M'-M)\mathfrak{M}'_{1M'}(i)\mathfrak{M}'_{1-M}(j)C_{2,M'-M}(\theta,\varphi)}{R^3}$$
$$=\gamma_i\gamma_j\hbar^2\left(\frac{\vec{I}_i\cdot\vec{I}_j}{R^3}-\frac{3(\vec{I}_i\cdot\vec{R})(\vec{I}_j\cdot\vec{R})}{R^5}\right)\,, \tag{8}$$

where, for example, the spherical nuclear magnetic-dipole components are

$$\mathfrak{M}'_{1,\pm1}(j)=\mp\tfrac{1}{2}\gamma_j\hbar[I_{jx}\pm iI_{jy}]\,,$$

where $\gamma\hbar$ replaces $(e\hbar/2mc)g_s$ in the definition of (3b). Also for $l=L=1$, Eq. (7) reduces to spin magnetic-dipole $[\mathfrak{M}'_1(j)=(e\hbar/mc)\vec{S}_j]$ and orbital magnetic-dipole $[\mathfrak{M}_1(i)=(e\hbar/2mc)\vec{L}_i]$ interaction. However, this is just one of the many terms contained in the conventional spin-other-orbit interaction.[35] This can be shown by making a two-center expansion of the r_{ij} expressions in the conventional spin-other-orbit (s.o.o.) interaction. By using the formula[18] for scalar and vector product, this interaction may be expressed as follows: $(\vec{r}_{ij}=-\vec{r}_{ji})$

$$H_{\text{s.o.o.}}=(1+P_{ij})\frac{e^2\hbar^2}{m^2c^2}\frac{\vec{S}_j\cdot\vec{r}_{ij}\times\vec{P}_i}{r_{ij}^3}=(1+\vec{P}_{ij})\frac{e^2\hbar^2}{m^2c^2}\sum_M(-)^M S_{j-M}\sum_R(+)\sqrt{2}\,i$$
$$\times\frac{C(111;k,M-k,M)r_{ij}C_{1k}(\theta_{ij}\varphi_{ij})P_{i,M-k}}{r_{ij}^3}\,, \tag{9}$$

where P_{ij} means permutation of i and j and $P_{i,M-k}$ is the $(M-k)$th spherical component of the momentum vector $\vec{P}_i$. In order to obtain

$$\vec{L}_{iM}=(\vec{r}_i\times\vec{P}_i)_M=\sum_k(-)\sqrt{2}\,i\,C(111;\,k,M-k,M)$$
$$\times r_i C_{1k}(\theta_i\varphi_i)P_{i,M-k}\,,\,,$$

we consider only the $t=2$, $q=0$ term in the following two-center expansion[7] with R along the Z axis:

$$\frac{C_{1k}(\theta_{ij}\varphi_{ij})}{r_{ij}^2} = \sum_{t=1}^{\infty}\sum_{q}\sum_{m}\left(\frac{(2t+2q+1)!}{(2t-2)!\,(2q)!\,3!}\right)^{1/2}(-)^t \times\frac{C(t+q,q,t;o,m,m)C(t-1,t,1;k-m,m,k)r_i^{t-1}r_j^q C_{t-1,k-m}(\theta_i\varphi_i)C_{q,m}(\theta_i\varphi_j)}{R^{(t+q+1)}}, \quad (10)$$

which is substituted into (9) giving

$$H_{\text{s.o.o.}} = \cdots + (1+P_{ij})\frac{e^2\hbar^2}{m^2c^2}\sum_{M}(-)^M S_{j-M}\sum_{k}(+)\sqrt{2}\,i \times\frac{C(111;k,M-k,M)(10)^{1/2}C(121;k,o,k)r_i C_{1,k}(\theta_i\varphi_i)P_{i,M-k}}{R^3}+\cdots, \quad (11)$$

where use was made of the fact that $C(202;000)=1$ and $C_{00}(\theta_j\varphi_j)=1$ and of the other symmetry properties of Clebsch-Gordan coefficients. Recoupling of angular momenta[18] through

$$C(121;kok)C(111;k,-M,-M+k)=\sum_f[3(2f+1)]^{1/2}W(1211;1f)C(21f;o,-M,-M) \times C(1f1;k,-M,k-M),$$

picking the $f=1$ term and using the symmetry of the Clebsch-Gordan coefficients, we get

$$H_{\text{s.o.o.}} = \cdots + (1+P_{ij})\frac{e^2\hbar^2}{m^2c^2}\left(\frac{3}{2}\right)^{1/2}\sum_{M}\frac{C(112;M,-M,o)S_{j-M}\sum_{k}(+)\sqrt{2}\,i\,C(111;k,M-k,M)r_i C_{1k}(\theta_i\varphi_i)P_{i,M-k}}{R^3}+\cdots$$

$$= \cdots + (1+P_{ij})\frac{e^2\hbar^2}{m^2c^2}\left(\frac{3}{2}\right)^{1/2}(-)\sum_{M}\frac{C(112;M,-M,o)(S_{j-M}L_{iM})}{R^3}+\cdots, \quad (12)$$

which contains the term identical to what would be obtained from Eq. (7) with $l=L=1$ and with $C_{l+L,M-M'}(o,\varphi)=C_{l+L,o}(o\varphi)=1$ when $\vec{R}$ is along Z.

These reductions to simple cases shown in Eqs. (8) and (12) serve to illustrate the nature of the general magnetic-multipole interaction operator derived in Eq. (7). For interaction between two atoms a and b or two molecules a and b, integrations over the wave functions of electron i in a and electron j in b are needed to obtain the corresponding magnetic-multipole moments. For interaction between two nuclei, $\mathfrak{M}'_{lM'}(j)$ and $\mathfrak{M}'_{LM}(i)$ refer to the nuclear spin magnetic-multipole moments of nuclei a and b, respectively.

ACKNOWLEDGMENTS

Publication of this work was supported in part by a Gulf Oil Foundation Grant given to the Department of Chemistry, The Catholic University of America, and by the Chemical Fund donated by Alumni and Friends of the Department. Thanks are due Maria Thomas for her patience and expertise in typing the manuscript.

[1] B. C. Carlson and G. S. Rushbrooke, Proc. Cambridge Philos. Soc. 46, 626 (1950).
[2] R. J. Buehler and J. O. Hirschfelder, Phys. Rev. 83, 628 (1951).
[3] M. E. Rose, J. Math. Phys. 37, 215 (1958).
[4] P. R. Fontana, J. Math. Phys. 2, 825 (1961).
[5] R. M. Pitzer, C. W. Kern, and W. N. Lipscomb, J. Chem. Phys. 37, 267 (1962).
[6] R. A. Sack, J. Math. Phys. 5, 260 (1964).
[7] Y.N. Chiu, J. Math. Phys. 5, 283 (1964).
[8] J. P. Dahl and M. P. Barnett, Mol. Phys. 9, 175 (1965).
[9] R. Nozawa, J. Math. Phys. 7, 1841 (1966).
[10] P. R. Fontana and W. J. Meath, J. Math. Phys. 9, 1357 (1968).
[11] K. G. Kay, H. P. Todd, and H. J. Silverstone, J. Chem. Phys. 51, 2363 (1969).
[12] H. Yasuda and T. Yamamoto, Prog. Theor. Phys. 45, 1458 (1971).
[13] M. Aubert-Frécon, J. Chem. Phys. 34, 341 (1978).
[14] R. L. Matcha, R. H. Pritchard, and C. W. Kern, J. Math. Phys. 12, 1155 (1971).
[15] R. L. Matcha, C. W. Kern, and D. M. Schrader, J. Chem. Phys. 51, 2152 (1969); R. L. Matcha and C. W. Kern, *ibid.* 51, 3434 (1969); R. L. Matcha, D. J. Kouri, and C. W. Kern, *ibid.* 53, 1052 (1970); R. L. Matcha, G. Malli, and Mac. B. Milleur, *ibid.* 56, 5982 (1972).
[16] J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (Wiley, New York, 1952), Appendix B.

[17]M. E. Rose, *Multipole Fields* (Wiley, New York, 1955).
[18]M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).
[19]D. M. Brink and G. R. Satchler, *Angular Momentum* (Oxford University, London, 1962), pp. 65–70 and 87–91.
[20]Y. N. Chiu, J. Chem. Phys. 45, 2969 (1966).
[21]C. Schwartz, Phys. Rev. 97, 380 (1955).
[22]H. Kopfermann, *Nuclear Moments* (Academic, New York, 1958); A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, London, 1961).
[23]C. Mavroyannis and M. J. Stephen, Mol. Phys. 5, 629 (1962); H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pergamon Oxford, 1969), pp. 219–221; W. J. Meath and J. O. Hirschfelder, J. Chem. Phys. 44 , 3197 (1966).
[24]D. P. Craig, E. A. Power, and T. Thirunamachandran, Chem. Phys. Lett. 6, 211 (1970); Proc. R. Soc. (London) A 322, 165 (1971).
[25]Y. N. Chiu (unpublished).
[26]R. J. Blin-Stoyle, *Theories of Nuclear Moments* (Oxford University, London, 1957).
[27]V. Jaccarino, J. G. King, R. A. Salten, and H. H. Stroke, Phys. Rev. 94, 1978 (1954); P. Kusch and T. G. Eck, *ibid.* 94, 1799 (1954).
[28]H. H. Brown and J. G. King, Phys. Rev. 142, 53 (1966).
[29]L. Y. C. Chiu, Chem. Phys. Lett. 49, 386 (1977), Eq. (4).
[30]Y. N. Chiu, J. Chem. Phys. 52, 3641 (1970).
[31]Y. N. Chiu, J. Chem. Phys. 55, 5053 (1971); 56, 5741 (1972).
[32]B. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963), pp. 87 and 88; *Angular Momentum Theory for Diatomic Molecules* (Academic, New York, 1975).
[33]B. L. Silver, *Irreducible Tensor Methods* (Academic, New York, 1976), pp. 109 and 110.
[34]Y. N. Chiu, J. Chem. Phys. 45, 2990 (1966), Eq. (A2).
[35]J. C. Slater, *Quantum Theory of Atomic Structure*, Vol. II (McGraw-Hill, New York, 1960), pp. 190–195; Y. N. Chiu, J. Chem. Phys. 48, 3476 (1968).