

Module I, Lecture 07: Spin Interaction Hamiltonians, part II

Reminder: time-independent perturbation theory

Magnetic interactions are weak compared to the kinetic and potential energy terms encountered in the common molecular electronic structure Hamiltonians. The standard approach for dealing with magnetic response properties of molecules is therefore perturbation theory. For the purposes of magnetic resonance, second-order PT expressions for the energy are sufficient.

Consider a system with a “large” Hamiltonian \hat{H}_0 for which eigenvalues and eigenfunctions are known:

$$\hat{H}_0 \left| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(0)} \right\rangle \quad (1)$$

For our purposes, \hat{H}_0 is the electronic structure Hamiltonian, including kinetic energy and Coulomb interaction terms. If a perturbation $\lambda \hat{H}_1$ is applied to the system, the perturbed wavefunctions and energies would have a Taylor expansion in the powers of its amplitude parameter λ :

$$\begin{aligned} \left| \psi_n \right\rangle &= \left| \psi_n^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle + \lambda^2 \left| \psi_n^{(2)} \right\rangle + \dots \\ E_n &= E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \end{aligned} \quad (2)$$

Substituting these expressions into the definition of the full system energy:

$$\begin{aligned} & \left(\hat{H}_0 + \lambda \hat{H}_1 \right) \left[\left| \psi_n^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle + \lambda^2 \left| \psi_n^{(2)} \right\rangle + \dots \right] = \\ & = \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right) \left[\left| \psi_n^{(0)} \right\rangle + \lambda \left| \psi_n^{(1)} \right\rangle + \lambda^2 \left| \psi_n^{(2)} \right\rangle + \dots \right] \end{aligned} \quad (3)$$

and equating the terms with equal powers of λ (Taylor expansion is unique), we get:

$$\begin{cases} \hat{H}_0 \left| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(0)} \right\rangle \\ \hat{H}_0 \left| \psi_n^{(1)} \right\rangle + \hat{H}_1 \left| \psi_n^{(0)} \right\rangle = E_n^{(0)} \left| \psi_n^{(1)} \right\rangle + E_n^{(1)} \left| \psi_n^{(0)} \right\rangle \\ \hat{H}_0 \left| \psi_n^{(2)} \right\rangle + \hat{H}_1 \left| \psi_n^{(1)} \right\rangle = E_n^{(0)} \left| \psi_n^{(2)} \right\rangle + E_n^{(1)} \left| \psi_n^{(1)} \right\rangle + E_n^{(2)} \left| \psi_n^{(0)} \right\rangle \\ \dots \end{cases} \quad (4)$$

The first equation we already know. Acting on the second and the third equation with $\left\langle \psi_n^{(0)} \right|$ yields:

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \right| \hat{H}_1 \left| \psi_n^{(0)} \right\rangle \quad E_n^{(2)} = \left\langle \psi_n^{(0)} \right| \hat{H}_1 \left| \psi_n^{(1)} \right\rangle - E_n^{(1)} \left\langle \psi_n^{(0)} \right| \psi_n^{(1)} \right\rangle \quad (5)$$

The first-order energy correction can be computed immediately. The second order energy correction requires the first-order correction to the wavefunction, which can be obtained, after quite a bit of algebra, from the second equation:

$$\left| \psi_n^{(1)} \right\rangle = \sum_{k \neq n} \frac{\left\langle \psi_k^{(0)} \right| \hat{H}_1 \left| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}} \left| \psi_k^{(0)} \right\rangle, \quad \left\langle \psi_n^{(1)} \right| \psi_n^{(0)} \right\rangle = 0 \quad (6)$$

With that in place, we obtain the final expression for the energy of the perturbed system to second order in the amplitude of the perturbation:

$$E_n = E_n^{(0)} + \left\langle \psi_n^{(0)} \right| \hat{H}_1 \left| \psi_n^{(0)} \right\rangle + \sum_{k \neq n} \frac{\left\langle \psi_n^{(0)} \right| \hat{H}_1 \left| \psi_k^{(0)} \right\rangle \left\langle \psi_k^{(0)} \right| \hat{H}_1 \left| \psi_n^{(0)} \right\rangle}{E_n^{(0)} - E_k^{(0)}} \quad (7)$$

Survey of interactions: g -tensor

The formalism that leads to the spin Hamiltonian for the interaction of an electron spin with the applied magnetic field is similar to that for the chemical shielding tensor. The energy operator for the electron dipole in an external magnetic field is

$$\hat{H}_G = \mu_B \hat{\vec{L}} \cdot \mathbf{g} \cdot \vec{B} \quad (8)$$

where $\hat{\vec{L}} = [\hat{L}_X \quad \hat{L}_Y \quad \hat{L}_Z]$ is the electron spin operator vector, \vec{B} is the magnetic induction vector, \mathbf{g} is a 3x3 matrix known as the g -tensor and the presence of Bohr magneton μ_B in front of the equation is historical. The components of the g -tensor are obtained by differentiating the ground state molecular energy, obtained from Equation (7), with respect to the Cartesian components of the electron magnetic moment and the applied magnetic field:

$$E = \vec{\mu}^{(e)} \cdot \mathbf{g} \cdot \vec{B}, \quad g_{nk} = \frac{\partial^2 E}{\partial \mu_n^{(e)} \partial B_k}, \quad \mathbf{g} = g_e \mathbf{1} + \Delta \mathbf{g} \quad (9)$$

where $\Delta \mathbf{g}$ is the deviation of the g -tensor from the free electron value g_e , which is a fundamental constant. After the derivatives are taken, the following perturbation terms survive in Equation (7):

$$\Delta \mathbf{g} = \langle \Psi_0 | \hat{H}^{\text{DS}} + \hat{H}^{\text{RZ}} | \Psi_0 \rangle - \frac{1}{2} \sum_{m=1}^{\infty} \frac{\langle \Psi_0 | \hat{H}^{\text{SO}} | \Psi_m \rangle \langle \Psi_m | \hat{L}_g | \Psi_0 \rangle + \langle \Psi_0 | \hat{L}_g | \Psi_m \rangle \langle \Psi_m | \hat{H}^{\text{SO}} | \Psi_0 \rangle}{E_0 - E_m} \quad (10)$$

The details of the Hamiltonians involved are beyond the scope of this course. The *diamagnetic shielding term* \hat{H}^{DS} is arising from the interaction between the vector potential of the external field and the vector potential of the electron dipole. The *relativistic Zeeman term* \hat{H}^{RZ} incorporates the relativistic correction to the interaction between electron magnetic moment and the applied magnetic field. The *spin-orbit coupling term* \hat{H}^{SO} includes the coupling between the magnetic moments associated with the orbital motion of the electrons and spins of both electrons and nuclei. The \hat{L}_g operator is simply the sum of electron angular momenta relative to the gauge origin.

In situations where any of the corresponding energies get outside the applicability range of perturbation theory or the relativistic effects cannot be ignored beyond $1/c^2$ terms (this often happens with paramagnetic metal clusters), more sophisticated theories must be used. Quantum mechanical calculations of g -tensors are normally performed using electronic structure theory software (Gaussian, ADF and ORCA being particularly noteworthy). For our purposes, only Equation (8) really matters and we simply require the g -tensor matrix as well as a schematic understanding of its physical origins.

Survey of interactions: isotropic hyperfine interaction

Isotropic HFC arises as the result of electron-nuclear *Fermi contact interaction*:

$$\hat{H}_{\text{FC}} = \frac{8\pi\hbar}{3} \gamma_e \gamma_n \rho(\vec{r}_n) (\hat{S}_e \cdot \hat{S}_n) \quad (11)$$

where γ_e and γ_n are magnetogyric ratios of the electron and the nucleus respectively, $\rho(\vec{r}_n)$ is the electron spin density at the nucleus point, \hat{S}_n are nuclear spin operators and \hat{S}_e are electron spin operators. This interaction has a complicated origin – it is an effective term that appears in the expression for the electron-nuclear dipolar interaction once the finite radius of the nucleus is taken into account. However, after the electronic structure theory calculation is finished, the spin Hamiltonian term is simple:

$$\hat{H}_{\text{FC}} = a \left(\hat{L}_X \hat{S}_X + \hat{L}_Y \hat{S}_Y + \hat{L}_Z \hat{S}_Z \right) \quad (12)$$

where a is the isotropic hyperfine coupling constant and the two sets of operators refer to the electron and the nuclear spin. Fermi contact interaction is isotropic – it does not change under rotations and is not averaged to zero in liquid state systems.

For historical reasons, hyperfine couplings are measured in units of magnetic field: in Gauss or milliTesla (1 mT = 10 Gauss). These indicate the magnetic field under which the free electron Zeeman frequency is equal to that hyperfine coupling. To convert magnetic field units into angular frequency units, multiply them by the free electron magnetogyric ratio. As a rule of thumb, a hyperfine coupling of 1 Gauss corresponds to the hyperfine coupling constant of 2.803 MHz or $17.609 \cdot 10^6$ in angular frequency units.

Survey of interactions: anisotropic hyperfine interaction

Unlike the inter-nuclear dipolar interaction (which is always axial, see the previous lecture) the electron-nuclear dipolar interaction can have a non-zero rhombicity because it involves a delocalized electron dipole. To obtain the Hamiltonian, the electron spin density distribution must be integrated over:

$$\hat{H}_{\text{DD}} = -\frac{\mu_0}{4\pi} \hbar \gamma_e \gamma_n \int \left(\frac{3(\hat{S}_e \cdot \vec{r}_{\text{en}})(\vec{r}_{\text{en}} \cdot \hat{S}_n) - (\hat{S}_e \cdot \hat{S}_n)}{r_{\text{en}}^5} - \frac{(\hat{S}_e \cdot \hat{S}_n)}{r_{\text{en}}^3} \right) \rho(\vec{r}_e) d^3 \vec{r}_e = \hat{S}_e \cdot \mathbf{A} \cdot \hat{S}_n \quad (13)$$

where γ_e and γ_n are magnetogyric ratios of the electron and the nucleus respectively, $\rho(\vec{r}_e)$ is the electron spin density, \hat{S}_e is a vector of electron spin operators, \hat{S}_n is a vector of nuclear spin operators, \vec{r}_{en} is the electron-nuclear distance vector and the integral is taken over the electron coordinates. Even though the rhombicity of this interaction is in general non-zero (the result of multiple axialities added together at different orientations), it is still traceless. The Hamiltonian in Equation (13) is often referred to as *anisotropic hyperfine interaction* – unlike the Fermi contact interaction described in the previous section, it does depend on the system orientation and does average to zero in non-viscous liquids.

Survey of interactions: inter-electron dipolar interaction

To obtain the *inter-electron dipolar interaction* tensor, the spatial distributions of \hat{S}_e of both electrons must be integrated over:

$$\hat{H}_{\text{DD}} = -\frac{\mu_0}{4\pi} \hbar \gamma_e^2 \iint \left(\frac{3(\hat{S}_1 \cdot \vec{r}_{12})(\vec{r}_{12} \cdot \hat{S}_2) - (\hat{S}_1 \cdot \hat{S}_2)}{r_{12}^5} - \frac{(\hat{S}_1 \cdot \hat{S}_2)}{r_{12}^3} \right) \rho(\vec{r}_1) \rho(\vec{r}_2) d^3 \vec{r}_1 d^3 \vec{r}_2 \quad (14)$$

where the integral is now taken over the coordinates of both electrons. If the two probability distributions do not overlap, the interaction is traceless, but has non-zero axiality and rhombicity. For electrons at distances greater than about 15 Angstrom, point dipole interaction is usually a good approximation.

Survey of interactions: exchange interaction

The exchange coupling is due to the non-classical part of the inter-electron Coulomb repulsion that happens to depend on spin. According to the fermion anti-symmetry constraint, a pair of electrons with spatial wavefunctions $\{\varphi_1(x), \varphi_2(x)\}$ and spin states $\{\alpha, \beta\}$ can be in four possible states:

$$\begin{aligned} & \frac{1}{\sqrt{2}}(\varphi_1(x_1)\varphi_2(x_2) + \varphi_2(x_1)\varphi_1(x_2)) \frac{\alpha\beta - \beta\alpha}{\sqrt{2}} \quad - \text{"singlet"} \\ \left\{ \begin{array}{c} \varphi_1(x) \\ \varphi_2(x) \end{array} \right\} \otimes \left\{ \begin{array}{c} \alpha \\ \beta \end{array} \right\} & \Rightarrow \frac{1}{\sqrt{2}}(\varphi_1(x_1)\varphi_2(x_2) - \varphi_2(x_1)\varphi_1(x_2)) \left\{ \begin{array}{c} \alpha\alpha \\ \frac{\alpha\beta + \beta\alpha}{\sqrt{2}} \\ \beta\beta \end{array} \right\} \quad - \text{"triplet"} \end{aligned} \quad (15)$$

The Coulomb interaction energy is different for the singlet and the triplet state:

$$\begin{aligned} & \frac{1}{2} \int (\varphi_1^*(x_1)\varphi_2^*(x_2) + \varphi_2^*(x_1)\varphi_1^*(x_2)) \frac{1}{r_{12}} (\varphi_1(x_1)\varphi_2(x_2) + \varphi_2(x_1)\varphi_1(x_2)) dV_1 dV_2 = \\ & = \int |\varphi_1(x_1)|^2 \frac{1}{r_{12}} |\varphi_2(x_2)|^2 dV_1 dV_2 + \int \varphi_1(x_1)\varphi_2^*(x_1) \frac{1}{r_{12}} \varphi_2(x_2)\varphi_1^*(x_2) dV_1 dV_2 \end{aligned} \quad (16)$$

$$\begin{aligned} & \frac{1}{2} \int (\varphi_1^*(x_1)\varphi_2^*(x_2) - \varphi_2^*(x_1)\varphi_1^*(x_2)) \frac{1}{r_{12}} (\varphi_1(x_1)\varphi_2(x_2) - \varphi_2(x_1)\varphi_1(x_2)) dV_1 dV_2 = \\ & = \int |\varphi_1(x_1)|^2 \frac{1}{r_{12}} |\varphi_2(x_2)|^2 dV_1 dV_2 - \int \varphi_1(x_1)\varphi_2^*(x_1) \frac{1}{r_{12}} \varphi_2(x_2)\varphi_1^*(x_2) dV_1 dV_2 \end{aligned}$$

The difference is $2J$, where J is the *exchange integral*:

$$J = \int \varphi_1(x_1)\varphi_2^*(x_1) \frac{1}{r_{12}} \varphi_2(x_2)\varphi_1^*(x_2) dV_1 dV_2 \quad (17)$$

Note the products of different wavefunctions depending on the same coordinate – for this interaction to be significant, there must be significant overlap between $\varphi_1(x)$ and $\varphi_2(x)$, otherwise the product $\varphi_1(x_1)\varphi_2^*(x_1)$ would go to zero. To accommodate this as a spin interaction, we must look at the effect that this interaction has in the spin space. The three triplet energy levels would have their energy reduced by J :

$$\langle T_0 | \hat{H}_J | T_0 \rangle = \langle T_{\pm} | \hat{H}_J | T_{\pm} \rangle = -J \quad (18)$$

and the singlet energy level is raised by J :

$$\langle S | \hat{H}_J | S \rangle = J \quad (19)$$

The singlet and the triplet are also the eigenfunctions of the Hamiltonian operator because it does not mix them. Using the projector expansion, we therefore get:

$$\hat{H}_X = J \frac{|\alpha\beta - \beta\alpha\rangle\langle\alpha\beta - \beta\alpha|}{2} - J |\alpha\alpha\rangle\langle\alpha\alpha| - J \frac{|\alpha\beta + \beta\alpha\rangle\langle\alpha\beta + \beta\alpha|}{2} - J |\beta\beta\rangle\langle\beta\beta| \quad (20)$$

When written in terms of the projection operators of individual spins, this transforms into:

$$\hat{H}_X = \left(\begin{array}{c|cccc} & |\alpha\alpha\rangle & |\alpha\beta\rangle & |\beta\alpha\rangle & |\beta\beta\rangle \end{array} \right) \begin{pmatrix} -J & 0 & 0 & 0 \\ 0 & 0 & J & 0 \\ 0 & J & 0 & 0 \\ 0 & 0 & 0 & -J \end{pmatrix} \begin{pmatrix} \langle\alpha\alpha| \\ \langle\alpha\beta| \\ \langle\beta\alpha| \\ \langle\beta\beta| \end{pmatrix} \quad (21)$$

We will shift the overall energy reference point (which is arbitrary anyway) by $J/2$ upwards to make this matrix traceless. The resulting coupling matrix:

$$\hat{H}_x = (|\alpha\alpha\rangle \quad |\alpha\beta\rangle \quad |\beta\alpha\rangle \quad |\beta\beta\rangle) \begin{pmatrix} -J/2 & 0 & 0 & 0 \\ 0 & J/2 & J & 0 \\ 0 & J & J/2 & 0 \\ 0 & 0 & 0 & -J/2 \end{pmatrix} \begin{pmatrix} \langle\alpha\alpha| \\ \langle\alpha\beta| \\ \langle\beta\alpha| \\ \langle\beta\beta| \end{pmatrix} \quad (22)$$

happens to be proportional to the matrix produced by the two-spin isotropic coupling Hamiltonian that we saw in the previous lecture (prove the equation below as an exercise):

$$\hat{L} \cdot \hat{S} = \hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z = \begin{pmatrix} 1/4 & 0 & 0 & 0 \\ 0 & -1/4 & 1/2 & 0 \\ 0 & 1/2 & -1/4 & 0 \\ 0 & 0 & 0 & 1/4 \end{pmatrix} \quad (23)$$

We can therefore conclude that the two-electron exchange interaction effectively manifests itself as an isotropic spin-spin coupling with the following Hamiltonian:

$$\hat{H}_x = -2J \hat{L} \cdot \hat{S} = -2J (\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y + \hat{L}_z \hat{S}_z) \quad (24)$$

The exchange interaction also has more complicated (but smaller) contributions which are not isotropic. From the algebraic perspective, these anisotropic contributions mix with the inter-electron dipolar coupling and zero-field splitting. The latter two are also, strictly speaking, not separate in their physical nature. For this reason, the three electron spin couplings (dipolar, exchange and ZFS) are often difficult to separate during the analysis of experimental data – the only reliable classification is algebraic.

Survey of interactions: zero-field splitting

The situation is more complicated when the unpaired electrons do overlap and the system consequently has to be described in terms of the total electron spin. The end result is an effective quadratic interaction of the total electron spin with itself, known as *zero field splitting*:

$$\hat{H}_{\text{ZFS}} = \hat{S} \cdot \mathbf{D} \cdot \hat{S} \quad (25)$$

The only universal definition of \mathbf{D} is via the derivative of the total molecular energy with respect to the components of the total electron dipole moment:

$$D_{ij} = \frac{\partial^2 E}{\partial \mu_i \partial \mu_j} \quad (26)$$

where i and j indices run over $\{x, y, z\}$. In very high-spin electron systems, fourth-order and higher field-independent terms may appear – a consequence of spin dynamics no longer being a small perturbation to the electronic structure theory Hamiltonian.

Visualization of spin interactions

It is often necessary to represent spin interactions in a visual form showing the orientation of the corresponding tensors relative to the molecular frame of reference. There are two primary schools of thought in this regard:

1. Ellipsoid plots: a sphere is drawn at an appropriate location (at the nucleus in the case of nucleus-centered interactions, such as CSA / HFC / NQI, and at the spin density centroid for the g -tensor and other electron spin interactions). The sphere is scaled by the absolute values of the

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three eigenvalues of the interaction tensor in the directions of the three corresponding eigenvectors. A set of axes is drawn inside the resulting ellipsoid, with red axes for positive eigenvalues and blue axes for the negative ones.

2. Spherical harmonic plots: the interaction is translated into the spherical tensor convention (see the previous lecture) and the spherical tensor coefficients are used as coefficients for the corresponding spherical harmonics. A spherical plot of the resulting function is generated at the nucleus in the case of nucleus-centered interactions, and at the spin density centroid for the g -tensor and other electron spin interactions.

Examples of both representations (generated by the interaction visualization module of the *Spinach* library) are shown below for the hyperfine coupling tensors of pyrene anion radical. Because the interactions themselves operate in a direct product of spin spaces that fundamentally have no classical analogue, the details of their visualization in Cartesian space are largely a matter of convenience.

