Electron-spin related properties and EPR

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Outline

- The EPR Hamiltonian
- Recalling the form of our electronic Hamiltonian
- The Heisenberg Hamiltonian
- Electron spin-Zeeman Hamiltonian
- Zero-field splittings
- Hyperfine interactions
- Other small contributions
In electron paramagnetic resonance it is the unpaired electron that takes center stage. Provides valuable information on distribution of unpaired electrons in a molecule (radical reactions). Provides a means to observe reactive intermediates. Strong resemblance to NMR in terms of the analysis of experiment, using an effective Hamiltonian. Major difference (computationally) is that whereas the nuclear spin functions could be manipulated independently of the electronic structure, a change in the electronic spin state leads to new wave functions. Quantum-chemical methods need to be able to properly treat spin states.
The magnetic field induces a splitting of the different electronic spin states, for half-integer spin systems like these, it is customary to refer to this as a Kramer’s pair.

- The radiation required to induce spin transitions corresponds to microwave radiation (same as rotational spectroscopy).
The information content in EPR spectroscopy

The diagram illustrates the energy levels and transitions in an electronic configuration, likely related to the ground state of a gaseous ion. The energy levels are labeled with angular momenta $^4A_2$, $^4F$, $^4T_2$, and $^4T_1$. The transitions are marked with $m_J$ values, indicating the magnetic quantum number. The table below the diagram lists the gaseous ion, $O_h$ crystal field, spin-orbit coupling (zero-field), and magnetic field ($\vec{H}$) configurations. The table entries are:

- **Gaseous Ion**: Various entries
- **$O_h$ Crystal Field**: Various entries
- **Spin-orbit Coupling (Zero-field)**: Various entries
- **Magnetic Field ($\vec{H}$)**: Various entries

The diagram and table together provide a comprehensive view of the energy transitions and quantum states in EPR spectroscopy.
The phenomenological EPR Hamiltonian can be written as

\[ \mathcal{H}^{\text{ESR}} = \mathcal{H}^\text{ex} + \mathcal{H}^\text{SZ} + \mathcal{H}^\text{ZFS} + \mathcal{H}^\text{hf} + \mathcal{H}^\text{nZ} + \mathcal{H}^\text{Nq} \]

- \( \mathcal{H}^\text{ex} \): Heisenberg Hamiltonian
- \( \mathcal{H}^\text{SZ} \): Electron spin–Zeeman interaction
- \( \mathcal{H}^\text{ZFS} \): Zero–field splitting
- \( \mathcal{H}^\text{hf} \): Hyperfine interactions
- \( \mathcal{H}^\text{nZ} \): Nuclear Zeeman interaction
- \( \mathcal{H}^\text{nq} \): Nuclear quadrupole interaction
Expanding the electronic Hamiltonian

- We recall that we have for the 1-electron Hamiltonian in the presence of external sources of magnetic fields and nuclear magnetic moments (implicit summation over electrons)

\[
H = H_0 + \left( [A_B + A_K]^T \cdot \mathbf{p} + B \cdot \mathbf{s} \right) + \frac{1}{2} \left( A_B^2 + 2A_B^T A_K + A_K^2 \right)
\]

\[
= H_0 + H^{10} + H^{01} + H^{11}_s + H^{01}_s + H^{20} + H^{11} + H^{02}
\]

- \( H^{BmK} \) here denotes the order in the perturbations \( B \) and \( m_K \)

- We note that \( B = \nabla \times A \), and thus we get

\[
(\nabla \times A_K) \cdot \mathbf{s} = \frac{8\pi \alpha^2}{3} \sum_K \delta(\mathbf{r}_K) m_K \cdot \mathbf{s} + \alpha^2 \sum_K \frac{3\mathbf{r}_K \cdot \mathbf{m}_K - r_k^2 \mathbf{m}_K}{r_k^5} \cdot \mathbf{s}
\]

- The first term referred to as the Fermi contact interaction
- The second term referred to as the spin-dipolar interaction
- Since they involve the electron spin, they are triplet operators
More details: First-order corrections

- $H^{10}$ denotes the orbital Zeeman interaction

\[ H^{10} = A \cdot p = \frac{1}{2} (B \times r_O) \cdot p = \frac{1}{2} B \cdot L_O \quad L_O = r_O \times p \]

- $H^{01}$ denotes the paramagnetic spin–orbit (PSO) interaction

\[ H^{01} = A_K \cdot p = \alpha^2 \sum_K m_K \frac{L_K}{r_K^3} \]

- In addition we have the Zeeman interaction

\[ H_{s}^{10} = B \cdot s \]

- and the triplet hyperfine interactions

\[ H_{s}^{01} = \frac{8\pi\alpha^2}{3} \sum_K \delta(r_K) m_K s + \alpha^2 \sum_K \frac{3r_K (r_K \cdot m_K) - r_K^2 m_K}{r_K^5} s = H^{FC} + H^{SD} \]
General remarks about contributions to the EPR Hamiltonian

- The operator for the electron spin will change the spin state of the molecule
- When considering contributing terms to the various observable interactions, we must ensure that spin symmetry also is preserved
- Important that wave function are stable towards triplet perturbing operators
- Most commonly used formalism is unrestricted approaches
- Spin-restricted methods are possible, but require that we allow the wave function to relax with respect to the triplet-perturbing operators
- Note also that degenerate perturbation theory must in many cases be used to analyze and calculate the properties
The form of the Heisenberg Hamiltonian is

\[ \mathcal{H}^{\text{ex}} = -2J \mathbf{s}_1 \cdot \mathbf{s}_2 \]

- Describes the (exchange) interaction between two different spin systems \( \mathbf{s}_1 \) and \( \mathbf{s}_2 \)
- \( J \) decreases exponentially with increasing separation of \( \mathbf{s}_1 \) and \( \mathbf{s}_2 \) since it depends on the overlap of the wavefunctions
- \( J > 0 \) corresponds to ferromagnetic spin arrangement (parallel), and \( J < 0 \) to anti-ferromagnetic spin arrangement (antiparallel)
- Energies for different spin arrangements much larger than the energies considered in EPR spectroscopy
Spin–Zeeman interaction

- The electron spin–Zeeman interaction Hamiltonian is given as

\[ \mathcal{H}^{sZ} = \mu_B S^T g \mathbf{B} \]

- \( S \) is here the effective spin of the system
Spin–Zeeman interaction

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\[ \mathcal{H}^{sZ} = \mu_B S^T gB \]

- \( S \) is here the effective spin of the system
- Recall that for systems with heavy elements, spin will no longer be a good quantum number
Spin–Zeeman interaction

- The electron spin–Zeeman interaction Hamiltonian is given as
  \[ \mathcal{H}^{sZ} = \mu_B S^T gB \]

- \( S \) is here the **effective spin** of the system
- Recall that for systems with heavy elements, spin will no longer be a good quantum number
- The operator is thus bilinear in the electron spin and the external magnetic field
- From our Hamiltonian, the Zeeman term is bilinear in the two perturbations
- We have an operator linear in the external magnetic field (orbital Zeeman)
- We have no operator linear in the electron spin coupling different electronic states
- Nonrelativistically, the spin-Zeeman interaction is thus
  \[ g = g_e 1 \quad g_e = -2.0023193043622, \quad m = -g_e \mu_B S / \hbar \]

- Identical for all systems
An important relativistic correction occurring in molecules is the spin–orbit coupling

\[
\hat{H}^{SO} = -\frac{e}{8\pi\epsilon_0 m_e} \alpha_{fs}^2 \left[ \sum_{iK} Z_K \frac{m_i \cdot l_{iK}}{r_{iK}^3} - \sum_{i \neq j} \frac{(m_i + 2m_j) \cdot l_{ij}}{r_{ij}^3} \right]
\]

\[
\equiv \hat{H}^{SO(1)} + \hat{H}^{SO(2)}
\]

Recall that \( l_{iK} = r_{iK} \times p_i \)

Introducing the minimal substitution, replacing \( p_i \rightarrow \pi_i = p_i + eA_i \), we also get

\[
\hat{H}^{SO,B} = \hat{H}^{SO,B(1)} + \hat{H}^{SO,B(2)}
\]

\[
\hat{H}^{SO,B(1)} = -\frac{e^2}{16\pi\epsilon_0 m_e} \alpha_{fs}^2 \left[ \sum_{iK} Z_K m_i \cdot \frac{(r_{iO} \cdot r_{iK})}{r_{iK}^3} \left( 1 - \frac{r_{iO} r_{iK}^T}{r_{iK}^3} \right) \cdot B \right]
\]

\[
\hat{H}^{SO,B(2)} = \frac{e^2}{16\pi\epsilon_0 m_e} \alpha_{fs}^2 \left[ \sum_{i \neq j} (m_i + 2m_j) \cdot \frac{(r_{iO} \cdot r_{ij})}{r_{ij}^3} \left( 1 - \frac{r_{iO} r_{ij}^T}{r_{ij}^3} \right) \cdot B \right]
\]
The relativistic electronic g tensor

- With interactions arising from relativistic corrections, we can write

\[ g = g_e \mathbf{1} + \Delta g \]

- The correction terms leading to the shift in the field free electron g tensor is

\[ \Delta g = \Delta g^{SO} + \Delta g^{RMC} + \Delta g^{GC} + \mathcal{O} \left( \alpha_{fs}^4 \right) \]

- The various contributions are defined as

\[
\begin{align*}
\Delta g^{SO}_{\alpha \beta} &= \frac{2}{\langle S_z \rangle_{\text{max}}} \langle \langle \hat{H}^B_{\alpha} ; \hat{H}^{SO}_{\beta} \rangle \rangle \\
\Delta g^{GC}_{\alpha \beta} &= \frac{2}{\langle S_z \rangle_{\text{max}}} \langle 0 | \hat{H}^{GC}_{\alpha \beta} | 0 \rangle = \frac{2}{\langle S_z \rangle_{\text{max}}} \langle 0 | \left( \hat{H}^{SO,B(1)} + \hat{H}^{SO,B(2)} \right)_{\alpha \beta} | 0 \rangle \\
\Delta g^{RMC}_{\alpha \beta} &= \frac{2}{\langle S_z \rangle_{\text{max}}} \langle 0 | \hat{H}^{SZ/KE}_{\alpha \beta} | 0 \rangle
\end{align*}
\]

- The last contribution is a relativistic correction to the spin–Zeeman interaction

\[ \hat{H}^{SZ/KE} = \frac{\alpha_{fs}^2}{2m_e^2} (\mathbf{m}_i \cdot \mathbf{B}) \pi_i^2 \]
The general analysis of open-shell systems is complicated. Limiting ourselves to a system with a single unpaired electron, the energy splitting is

$$\Delta E = \mu_B \sqrt{B^T G B}$$

$G = g \cdot g^T$ is the so-called symmetric $g$ tensor. $G$ and $g$ provide the same information.

We can consider the shift in the $g_e$ tensor as due to the local magnetic field experienced by the unpaired electron due to the electronic structure of the molecules.

Of these three contributions, the spin–orbit contribution to the electronic $g$ tensor dominates in (almost) all cases.

Calculation must ensure that the wave function can handle the triplet perturbing operators.
g tensors in dihalogen radicals

- If we include higher-order relativistic contributions, a number of additional contributions appear.
- Can quickly become sizeable, in particular if spin-orbit effects are quenched.

<table>
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<tr>
<th>molecule</th>
<th>method</th>
<th>$\Delta g_x$ (in ppt)</th>
<th>$\Delta g_y$ (in ppt)</th>
<th>$\Delta g_z$ (in ppt)</th>
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<td>nonrel$^a$ rel$^b$ total</td>
<td>nonrel$^a$ rel$^b$ total</td>
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<td>nonrel$^a$ rel$^b$ total</td>
<td>nonrel$^a$ rel$^b$ total</td>
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<td>expt$^h$</td>
<td>- - -</td>
<td>- - -</td>
<td>expt$^h$</td>
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</table>

Zero-field splittings (ZFS)

- The ZFS is a measure of the coupling between two unpaired electrons.
- Causes a splitting of a $2S + 1$-spin degenerate state $\Psi_0$.
- Is always present, also in the absence of an external magnetic field.
- Represents the EPR analogue of the spin–spin coupling constants.
- The energy splittings determined from the eigenvalues of the matrix

$$| H_{ij}^{ZFS} - W\delta_{ij} | = 0$$
Two contributions (assuming here a triplet reference state)

\[ H_{i,j} = \langle ^{2S+1}\psi_0^i | H_{ss} | ^{2S+1}\psi_0^j \rangle - \sum_{n,\lambda} \sum_k \langle ^{2S+1}\psi_0^i | H_{so} | \lambda \psi_n^k \rangle \langle \lambda \psi_n^k | H_{so} | ^{2S+1}\psi_0^j \rangle \frac{\lambda E_n}{E_0} - 3 E_0 \]

- \( H_{ss} \) is the electron spin–spin interaction operator (dipolar interaction)

\[ H_{ss} = \frac{\alpha^2}{2} \sum_{i,j} \left[ \frac{\vec{s}_i \cdot \vec{s}_j}{r_{i,j}^3} - \frac{3(\vec{s}_i \cdot \vec{r}_{i,j})(\vec{s}_j \cdot \vec{r}_{i,j})}{r_{ij}^5} \right] \]

- \( H_{so} \) is the one- and two-electron spin–orbit operator

\[ H_{so} = \frac{\alpha^2}{2} \left[ \sum_{i,K} Z_K \frac{\vec{l}_{ik} \cdot \vec{s}_i}{r_{iK}^3} - \sum_{ij} \frac{\vec{l}_{ij} \cdot (\vec{s}_i + 2\vec{s}_j)}{r_{ij}^3} \right] \]
In a diagonal basis, it is customary to write the ZFS effective Hamiltonian as

\[ H_{ZFS} = D \left( S_z^2 - \frac{1}{3} S^2 \right) + E \left( S_x^2 - S_y^2 \right) \]

- Two independent parameters that affect the EPR spectrum (the isotropic contribution do not contribute to the splitting of the spin sublevels)
- The ZFS is in most cases dominated by the spin–orbit contribution (spin–spin interactions mediated by the electrons)
- In organic radicals, the spin–spin dipolar interaction may be the dominant contribution (but it is small)
Solvent effects on ZFS

- It has been experimentally observed that the solvent shift on the ZFS depends linearly on $\Delta E_{T\rightarrow S}$:
  - Solvent-induced mixing of different triplet states?
  - The changes in the ZFS is due to changes in the spin–orbit contribution due to changes in $\Delta E_{T\rightarrow S}$?
- MCSCF: 8 electrons in 7(8) orbitals ($\sigma$ and $\pi$-type)
ZFS of $^3B_2$ state of pyridine

<table>
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<tr>
<th>ZFS</th>
<th>Gas</th>
<th>Aniline</th>
<th>Ethanol</th>
<th>Nitromethane</th>
<th>Water</th>
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<td>-0.1626</td>
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<td>$E_{ssc}$</td>
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<td>-0.0175</td>
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<td>$D_{soc}$</td>
<td>0.005</td>
<td></td>
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</table>

All results reported in cm$^{-1}$, using a TZ basis of Dunning


- Spin-orbit contribution very small in the gas-phase and thus not likely to explain the solvent dependence
- Can we explain the solvent shift from the spin–spin contribution only?
ZFS of $^3A''$ state of quinoline
The hyperfine interactions provide very detailed information about the electronic structure of a molecule. Couples the magnetic moment of the electrons to the magnetic moments of the nuclei

\[ \mathcal{H}_{\text{hf}} = \sum_K \left( A^{\text{fc}}_K S^T \cdot I_K + S^T A^{\text{sd}}_K I_K \right) \]

Two contributions, both arising from bilinear terms in the Hamiltonian
The interaction operators for the hyperfine tensors

- The Fermi contact contribution is given as

\[
A_{K}^{\text{fc}} = -\frac{1}{2} g_K g_e \mu_B \mu_N \langle S_Z \rangle^{-1} \sum_{\mu\nu} \left\langle \phi_\mu \left| \hat{H}_{K}^{(FC)} \right| \phi_\nu \right\rangle D^\alpha_{\mu\nu} - \beta 
\]

- The spin-dipolar contribution is given as

\[
A_{K}^{\text{sd}} = -\frac{1}{2} g_K g_e \mu_B \mu_N \langle S_Z \rangle^{-1} \sum_{\mu\nu} \left\langle \phi_\mu \left| \hat{H}_{K}^{(SD)} \right| \phi_\nu \right\rangle D^\alpha_{\mu\nu} - \beta 
\]

- Gives information about the spin density (difference between \(\alpha\) and \(\beta\) densities) in molecules
- The same operators appear in the calculation of spin–spin coupling constants in NMR, but not as expectation value contributions
Comments on the calculation of hyperfine interactions

- Tight basis functions needed in order to describe the Fermi contact contribution (spin density at the nucleus)
- We need to be able to describe accurately the spin density (easiest is unrestricted method, but spin not a good quantum number)
- Spin contamination effects remain unclear

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Isotope</th>
<th>BP86</th>
<th>BLYP</th>
<th>B3LYP</th>
<th>UBP86</th>
<th>UBLYP</th>
<th>UB3LYP</th>
<th>Expt.</th>
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<td>8.3(4), 8.0(4)</td>
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<td>-4.1</td>
<td>-5.1</td>
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</table>

Nuclear Zeeman interaction and nuclear quadrupole contributions

Due to the inherent line broadening occurring because of the unpaired electron(s), these latter two terms are in most cases not observed.

The nuclear Zeeman term is the shielding constant, but conventionally in EPR spectroscopy reported in terms of modified nuclear g factors

\[ \mathcal{H}^{nz} = -\mu_N \sum_K g_K \mathbf{B}^T \cdot \mathbf{l}_K \]

The nuclear quadrupole contribution involves the nuclear spins squared

\[ \mathcal{H}^{Nq} = \frac{1}{2} \sum_K \frac{-eQ_K}{l_K(2l_K - 1)} \mathbf{l}_K^T \mathbf{V}^K \mathbf{l}_K \]
In EPR spectroscopy, transitions between different electron spin sublevels are measured.

Transition energies are in the microwave region, overlapping with rotational spectroscopy (thus other transitions may also be observed).

Requires adequate treatment of open-shell wave functions of different multiplicity.

DFT performs well for selected properties, in particular for hyperfine interactions.

For more complicated properties such as zero-field splitting parameters, wave-function based methods appear (at present) to be the only viable option.