Molecules in Magnetic Fields

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Sections

Section 1

Electronic Hamiltonian

Hamiltonian Mechanics

▶ In classical Hamiltonian mechanics, a system of particles is described in terms of their positions q_i and conjugate momenta p_i.

▶ For each system, there exists a scalar Hamiltonian function $H(q_i, p_i)$ such that the classical equations of motion are given by:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \text{(Hamilton's equations)}$$

   ▶ note: the Hamiltonian H is not unique!

▶ Example: a single particle of mass m in a conservative force field $F(q)$

   ▶ the Hamiltonian is constructed from the corresponding scalar potential:

$$H(q, p) = \frac{p^2}{2m} + V(q), \quad F(q) = -\frac{\partial V(q)}{\partial q}$$

   ▶ Hamilton's equations of motion are equivalent to Newton's equations:

$$\left.\begin{array}{l} \dot{q} = \frac{\partial H(q,p)}{\partial p} = \frac{p}{m} \\ \dot{p} = -\frac{\partial H(q,p)}{\partial q} = -\frac{\partial V(q)}{\partial q} \end{array}\right\} \implies m\ddot{q} = F(q) \quad \text{(Newton's equations)}$$

   ▶ Hamilton's equations are first-order differential equations – Newton's are second-order

Quantization of a Particle in a Conservative Force Field

▶ The Hamiltonian formulation is more general than the Newtonian formulation:

  ▶ it is invariant to coordinate transformations
  ▶ it provides a uniform description of matter and field
  ▶ it constitutes the springboard to quantum mechanics

▶ The Hamiltonian function (total energy) of a particle in a conservative force field:

$$H(q, p) = \frac{p^2}{2m} + V(q)$$

▶ Standard rule for quantization (in Cartesian coordinates):

  ▶ carry out the operator substitutions

$$\mathbf{p} \to -i\hbar \boldsymbol{\nabla}, \quad H \to i\hbar \frac{\partial}{\partial t}$$

  ▶ multiply the resulting expression by the wave function $\Psi(q)$ from the right:

$$i\hbar \frac{\partial \Psi(q)}{\partial t} = \left[-\frac{\hbar^2}{2m} \nabla^2 + V(q) \right] \Psi(q)$$

▶ This approach is sufficient for a treatment of electrons in an electrostatic field

  ▶ it is insufficient for nonconservative systems
  ▶ it is therefore inappropriate for systems in a general electromagnetic field

Lorentz Force and Maxwell's Equations

▶ In the presence of an electric field $\mathbf{E}$ and a magnetic field (magnetic induction) $\mathbf{B}$,
a classical particle of charge z experiences the Lorentz force:

$$\mathbf{F} = z\,(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

  ▶ since this force depends on the velocity $\mathbf{v}$ of the particle, it is not conservative

▶ The electric and magnetic fields $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$ satisfy Maxwell's equations (1861–1868):

$$\boldsymbol{\nabla} \cdot \mathbf{E} = \rho/\varepsilon_0 \quad \leftarrow \text{Coulomb's law}$$
$$\boldsymbol{\nabla} \times \mathbf{B} - \varepsilon_0 \mu_0\, \partial\mathbf{E}/\partial t = \mu_0 \mathbf{J} \quad \leftarrow \text{Ampère's law with Maxwell's correction}$$
$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0$$
$$\boldsymbol{\nabla} \times \mathbf{E} + \partial\mathbf{B}/\partial t = \mathbf{0} \quad \leftarrow \text{Faraday's law of induction}$$

where $\rho(\mathbf{r}, t)$ and $\mathbf{J}(\mathbf{r}, t)$ are the charge and current densities, respectively

▶ Note:

  ▶ when ρ and $\mathbf{J}$ are known, Maxwell's equations can be solved for $\mathbf{E}$ and $\mathbf{B}$
  ▶ but the particles are driven by the Lorentz force, so ρ and $\mathbf{J}$ are functions of $\mathbf{E}$ and $\mathbf{B}$

▶ We here consider the motion of particles in a given (fixed) electromagnetic field

Scalar and Vector Potentials

▶ The second, homogeneous pair of Maxwell's equations involves only **E** and **B**:

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0 \tag{1}$$

$$\boldsymbol{\nabla} \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = \mathbf{0} \tag{2}$$

1. Eq. (1) is satisfied by introducing the vector potential **A**:

$$\boldsymbol{\nabla} \cdot \mathbf{B} = 0 \quad \Longrightarrow \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} \qquad \leftarrow \text{vector potential} \tag{3}$$

2. inserting Eq. (3) in Eq. (2) and introducing a scalar potential ϕ, we obtain

$$\boldsymbol{\nabla} \times \left(\mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} \right) = \mathbf{0} \quad \Longrightarrow \quad \mathbf{E} + \frac{\partial \mathbf{A}}{\partial t} = -\boldsymbol{\nabla} \phi \qquad \leftarrow \text{scalar potential}$$

▶ The second pair of Maxwell's equations is thus automatically satisfied by writing

$$\mathbf{E} = -\boldsymbol{\nabla} \phi - \frac{\partial \mathbf{A}}{\partial t}$$
$$\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

▶ The potentials $(\phi, \mathbf{A})$ contain four rather than six components as in $(\mathbf{E}, \mathbf{B})$.

▶ ϕ and **A** are obtained by solving the inhomogeneous pair of Maxwell's equations, containing ρ and **J**

Gauge Transformations

▶ Consider the following gauge transformation of the potentials:

$$\left.\begin{array}{rcl} \phi' & = & \phi - \frac{\partial f}{\partial t} \\ \mathbf{A}' & = & \mathbf{A} + \boldsymbol{\nabla} f \end{array}\right\} \text{ with } f = f(q, t) \leftarrow \text{gauge function of position and time}$$

▶ Such a transformation of the potentials does not affect the physical fields:

$$\mathbf{E}' = -\boldsymbol{\nabla}\phi' - \frac{\partial \mathbf{A}'}{\partial t} = -\boldsymbol{\nabla}\phi + \boldsymbol{\nabla}\frac{\partial f}{\partial t} - \frac{\partial \mathbf{A}}{\partial t} - \frac{\partial \boldsymbol{\nabla} f}{\partial t} = \mathbf{E}$$

$$\mathbf{B}' = \boldsymbol{\nabla} \times \mathbf{A}' = \boldsymbol{\nabla} \times (\mathbf{A} + \boldsymbol{\nabla} f) = \mathbf{B} + \boldsymbol{\nabla} \times \boldsymbol{\nabla} f = \mathbf{B}$$

▶ Conclusion: the scalar and vector potentials ϕ and $\mathbf{A}$ are not unique

  ▶ we are free to choose $f(q, t)$ to make the potentials satisfy additional conditions
  ▶ typically, we require the vector potential to be divergenceless:

$$\boldsymbol{\nabla} \cdot \mathbf{A}' = 0 \implies \boldsymbol{\nabla} \cdot (\mathbf{A} + \boldsymbol{\nabla} f) = 0 \implies \nabla^2 f = -\boldsymbol{\nabla} \cdot \mathbf{A} \quad \leftarrow \text{Coulomb gauge}$$

▶ We shall always assume that the vector potential satisfies the Coulomb gauge:

$$\boxed{\boldsymbol{\nabla} \times \mathbf{A} = \mathbf{B}, \quad \boldsymbol{\nabla} \cdot \mathbf{A} = 0 \quad \leftarrow \text{Coulomb gauge}}$$

  ▶ note: $\mathbf{A}$ is still not uniquely determined, the following transformation being allowed:

$$\mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} f, \quad \nabla^2 f = 0$$

Hamiltonian in an Electromagnetic Field

▶ We must construct a Hamiltonian function such that
Hamilton's equations are equivalent to Newton's equation with the Lorentz force:

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \& \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \Longleftrightarrow \quad m\mathbf{a} = z\left(\mathbf{E} + \mathbf{v} \times \mathbf{B}\right)$$

▶ To this end, we introduce scalar and vector potentials ϕ and $\mathbf{A}$ such that

$$\mathbf{E} = -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A}$$

▶ In terms of these potentials, the classical Hamiltonian function becomes

$$H = \frac{\pi^2}{2m} + z\phi, \quad \boldsymbol{\pi} = \mathbf{p} - z\mathbf{A} \quad \leftarrow \text{kinetic momentum}$$

▶ Quantization is then accomplished in the usual manner, by the substitutions

$$\mathbf{p} \to -i\hbar\boldsymbol{\nabla}, \quad H \to i\hbar\frac{\partial}{\partial t}$$

▶ The time-dependent Schrödinger equation for a particle in an electromagnetic field:

$$i\hbar\frac{\partial \Psi}{\partial t} = \frac{1}{2m}\left(-i\hbar\boldsymbol{\nabla} - z\mathbf{A}\right) \cdot \left(-i\hbar\boldsymbol{\nabla} - z\mathbf{A}\right)\Psi + z\phi\,\Psi$$

Electron Spin

▶ The nonrelativistic Hamiltonian for an electron in an electromagnetic field is then given by:

$$H = \frac{\pi^2}{2m} - e\phi, \quad \boldsymbol{\pi} = -i\hbar\boldsymbol{\nabla} + e\mathbf{A}$$

▶ However, this description ignores a fundamental property of the electron: spin.

▶ Spin was introduced by Pauli in 1927, to fit experimental observations:

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m}\mathbf{B} \cdot \boldsymbol{\sigma} - e\phi$$

where $\boldsymbol{\sigma}$ contains three operators, represented by the two-by-two Pauli spin matrices

$$\sigma_x = \left(\begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right), \quad \sigma_y = \left(\begin{array}{cc} 0 & -i \\ i & 0 \end{array} \right), \quad \sigma_z = \left(\begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right)$$

▶ The Schrödinger equation now becomes a two-component equation:

$$\begin{pmatrix} \frac{\pi^2}{2m} - e\phi + \frac{e\hbar}{2m}B_z & \frac{e\hbar}{2m}\left(B_x - iB_y\right) \\ \frac{e\hbar}{2m}\left(B_x + iB_y\right) & \frac{\pi^2}{2m} - e\phi - \frac{e\hbar}{2m}B_z \end{pmatrix} \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix} = E \begin{pmatrix} \Psi_\alpha \\ \Psi_\beta \end{pmatrix}$$

▶ Note: the two components are coupled only in the presence of an external magnetic field

Spin and Relativity

- The introduction of spin by Pauli in 1927 may appear somewhat ad hoc
- By contrast, spin arises naturally from Dirac's relativistic treatment in 1928
    - is spin a relativistic effect?
- However, reduction of Dirac's equation to nonrelativistic form yields the Hamiltonian

$$H = \frac{(\boldsymbol{\sigma} \cdot \boldsymbol{\pi})^2}{2m} - e\phi = \frac{\pi^2}{2m} + \frac{e\hbar}{2m}\mathbf{B} \cdot \boldsymbol{\sigma} - e\phi \neq \frac{\pi^2}{2m} - e\phi$$

    - in this sense, spin is not a relativistic property of the electron
    - on the other hand, in the nonrelativistic limit, all magnetic fields disappear. . .
- We interpret $\boldsymbol{\sigma}$ by associating an intrinsic angular momentum (spin) with the electron:

$$\mathbf{s} = \hbar\boldsymbol{\sigma}/2$$

Molecular Electronic Hamiltonian

- The nonrelativistic Hamiltonian for an electron in an electromagnetic field is therefore

$$H = \frac{\pi^2}{2m} + \frac{e}{m}\mathbf{B}\cdot\mathbf{s} - e\phi, \quad \boldsymbol{\pi} = \mathbf{p} + e\mathbf{A}, \quad \mathbf{p} = -i\hbar\boldsymbol{\nabla}$$

- expanding π^2 and assuming the Coulomb gauge $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$, we obtain

$$\pi^2\Psi = (\mathbf{p} + e\mathbf{A})\cdot(\mathbf{p} + e\mathbf{A})\,\Psi = p^2\Psi + e\mathbf{p}\cdot\mathbf{A}\Psi + e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi$$

$$= p^2\Psi + e(\mathbf{p}\cdot\mathbf{A})\Psi + 2e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi = \left(p^2 + 2e\mathbf{A}\cdot\mathbf{p} + e^2A^2\right)\Psi$$

- in molecules, the dominant electromagnetic contribution is from the nuclear charges:

$$\phi = -\frac{1}{4\pi\epsilon_0}\sum_K \frac{Z_K e}{r_K} + \phi_{\text{ext}}$$

- Summing over all electrons and adding pairwise Coulomb interactions, we obtain

$$
\begin{aligned}
H = &\sum_i \frac{1}{2m}p_i^2 - \frac{e^2}{4\pi\epsilon_0}\sum_{Ki}\frac{Z_K}{r_{iK}} + \frac{e^2}{4\pi\epsilon_0}\sum_{i>j}r_{ij}^{-1} && \leftarrow \text{zero-order Hamiltonian} \\
&+ \frac{e}{m}\sum_i \mathbf{A}_i\cdot\mathbf{p}_i + \frac{e}{m}\sum_i \mathbf{B}_i\cdot\mathbf{s}_i - e\sum_i \phi_i && \leftarrow \text{first-order Hamiltonian} \\
&+ \frac{e^2}{2m}\sum_i A_i^2 && \leftarrow \text{second-order Hamiltonian}
\end{aligned}
$$

Magnetic Perturbations

▶ In atomic units, the molecular Hamiltonian is given by

$$H = H_0 + \underbrace{\sum_i \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i}_{\text{orbital paramagnetic}} + \underbrace{\sum_i \mathbf{B}(\mathbf{r}_i) \cdot \mathbf{s}_i}_{\text{spin paramagnetic}} - \sum_i \phi(\mathbf{r}_i) + \underbrace{\frac{1}{2} \sum_i A^2(\mathbf{r}_i)}_{\text{diamagnetic}}$$

▶ There are two kinds of magnetic perturbation operators:
  ▶ the paramagnetic operator is linear and may lower or raise the energy
  ▶ the diamagnetic operator is quadratic and always raises the energy

▶ There are two kinds of paramagnetic operators:
  ▶ the orbital paramagnetic operator couples the field to the electron's orbital motion
  ▶ the spin paramagnetic operator couples the field to the electron's spin

▶ In the study of magnetic properties, we are interested in two types of perturbations:
  ▶ uniform external magnetic field $\mathbf{B}$, with vector potential

$$\mathbf{A}_{\text{ext}}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r} \quad \text{leads to Zeeman interactions}$$

  ▶ nuclear magnetic moments $\mathbf{M}_K$, with vector potential

$$\mathbf{A}_{\text{nuc}}(\mathbf{r}) = \alpha^2 \sum_K \frac{\mathbf{M}_K \times \mathbf{r}_K}{r_K^3} \quad \text{leads to hyperfine interactions}$$

  where $\alpha \approx 1/137$ is the fine-structure constant

Section 2

Uniform Magnetic Fields and London Orbitals

Hamiltonian in a Uniform Magnetic Field

▶ The nonrelativistic electronic Hamiltonian (implied summation over electrons):

$$H = H_0 + \mathbf{A}(\mathbf{r}) \cdot \mathbf{p} + \mathbf{B}(\mathbf{r}) \cdot \mathbf{s} + \tfrac{1}{2} A(\mathbf{r})^2$$

▶ The vector potential of the uniform field $\mathbf{B}$ is given by:

$$\boxed{\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} = \text{const} \implies \mathbf{A_O}(\mathbf{r}) = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) = \tfrac{1}{2}\mathbf{B} \times \mathbf{r_O}}$$

  ▶ note: the gauge origin $\mathbf{O}$ is arbitrary!

▶ The orbital paramagnetic interaction becomes:

$$\mathbf{A_O}(\mathbf{r}) \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \cdot (\mathbf{r} - \mathbf{O}) \times \mathbf{p} = \tfrac{1}{2}\mathbf{B} \cdot \mathbf{L_O}$$

where we have introduced the angular momentum relative to the gauge origin:

$$\mathbf{L_O} = \mathbf{r_O} \times \mathbf{p}$$

▶ The diamagnetic interaction becomes:

$$\tfrac{1}{2}A_\mathbf{O}^2(\mathbf{r}) = \tfrac{1}{8}(\mathbf{B} \times \mathbf{r_O}) \cdot (\mathbf{B} \times \mathbf{r_O}) = \tfrac{1}{8}\left[B^2 r_\mathbf{O}^2 - (\mathbf{B} \cdot \mathbf{r_O})^2\right]$$

▶ The electronic Hamiltonian in a uniform magnetic field depends on the gauge origin:

$$H = H_0 + \frac{1}{2}\mathbf{B} \cdot \mathbf{L_O} + \mathbf{B} \cdot \mathbf{s} + \frac{1}{8}\left[B^2 r_\mathbf{O}^2 - (\mathbf{B} \cdot \mathbf{r_O})^2\right]$$

  ▶ as we shall see, a change of the origin is a gauge transformation

Gauge Transformation of Schrödinger Equation

▶ What is the effect of a gauge transformation on the wave function?

▶ Consider a general gauge transformation for the electron (atomic units):

$$\mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla} f, \quad \phi' = \phi - \frac{\partial f}{\partial t}$$

▶ It can be shown that this represents a unitary transformation of $H - \mathrm{i}\partial/\partial t$:

$$\left(H' - \mathrm{i}\frac{\partial}{\partial t}\right) = \exp\left(-\mathrm{i}f\right)\left(H - \mathrm{i}\frac{\partial}{\partial t}\right)\exp\left(\mathrm{i}f\right)$$

▶ In order that the Schrödinger equation is still satisfied

$$\left(H' - \mathrm{i}\frac{\partial}{\partial t}\right)\Psi' = 0 \quad \Longleftrightarrow \quad \left(H - \mathrm{i}\frac{\partial}{\partial t}\right)\Psi = 0,$$

the wave function undergoes a compensating unitary transformation:

$$\Psi' = \exp\left(-\mathrm{i}f\right)\Psi$$

▶ All observable properties such as the electron density are then unaffected:

$$\rho' = (\Psi')^*\Psi' = [\Psi\exp(-\mathrm{i}f)]^*[\exp(-\mathrm{i}f)\Psi] = \Psi^*\Psi = \rho$$

Gauge-Origin Transformations

▶ Different choices of origin in $\mathbf{A_O}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O})$ are related by gauge transformations:
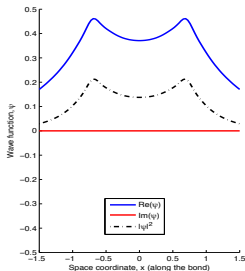
$$\mathbf{A_G}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{G}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) - \frac{1}{2}\mathbf{B} \times (\mathbf{G} - \mathbf{O})$$
$$= \mathbf{A_O}(\mathbf{r}) - \mathbf{A_O}(\mathbf{G}) = \mathbf{A_O}(\mathbf{r}) + \boldsymbol{\nabla} f, \quad f(\mathbf{r}) = -\mathbf{A_O}(\mathbf{G}) \cdot \mathbf{r}$$

▶ The exact wave function transforms accordingly and gives gauge-invariant results:

$$\Psi_{\mathbf{G}}^{\text{exact}} = \exp\left[-\mathrm{i}f(\mathbf{r})\right]\Psi_{\mathbf{O}}^{\text{exact}} = \exp\left[\mathrm{i}\mathbf{A_O}(\mathbf{G})\cdot\mathbf{r}\right]\Psi_{\mathbf{O}}^{\text{exact}} \qquad \text{(rapid) oscillations}$$

▶ Illustration: H_2 on the z axis in a magnetic field $B = 0.2\,\text{a.u.}$ in the y direction

    ▶ wave function with gauge origin at $\mathbf{O} = (0, 0, 0)$ (left) and $\mathbf{G} = (100, 0, 0)$ (right)
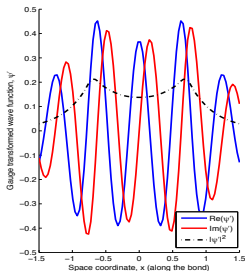
London Orbitals

▶ The exact wave function transforms in the following manner:

$$\Psi_{\mathbf{G}}^{\text{exact}} = \exp\left[i\tfrac{1}{2}\mathbf{B} \times (\mathbf{G} - \mathbf{O}) \cdot \mathbf{r}\right] \Psi_{\mathbf{O}}^{\text{exact}}$$

  ▶ this behaviour cannot easily be modelled by combinations of standard atomic orbitals

▶ Let us instead build this behaviour directly into the atomic orbitals:

$$\omega_{lm}(\mathbf{r}_K, \mathbf{B}, \mathbf{G}) = \exp\left[i\tfrac{1}{2}\mathbf{B} \times (\mathbf{G} - \mathbf{K}) \cdot \mathbf{r}\right] \chi_{lm}(\mathbf{r}_\mathbf{K})$$

  ▶ $\chi_{lm}(\mathbf{r}_K)$ is a normal atomic orbital centred at $\mathbf{K}$ and with quantum numbers lm
  ▶ $\omega_{lm}(\mathbf{r}_K, \mathbf{B}, \mathbf{G})$ is a field-dependent orbital at $\mathbf{K}$ with field $\mathbf{B}$ and gauge origin $\mathbf{G}$

▶ Each AO now responds in a physically sound manner to an applied magnetic field

  ▶ indeed, all AOs are now correct to first order in $\mathbf{B}$, for any gauge origin $\mathbf{G}$
  ▶ the calculations become rigorously gauge-origin independent
  ▶ uniform (good) quality follows, independent of molecule size

▶ These are the London orbitals after Fritz London (1937)

  ▶ also known as GIAOs (gauge-origin independent AOs or gauge-origin including AOs)

▶ Question:

  ▶ are London orbitals needed in atoms?

Dissociation With and Without London Orbitals

▶ Let us consider the FCI dissociation of H_2 in a magnetic field
  ▶ full lines: with London atomic orbitals
  ▶ dashed lines: without London atomic orbitals
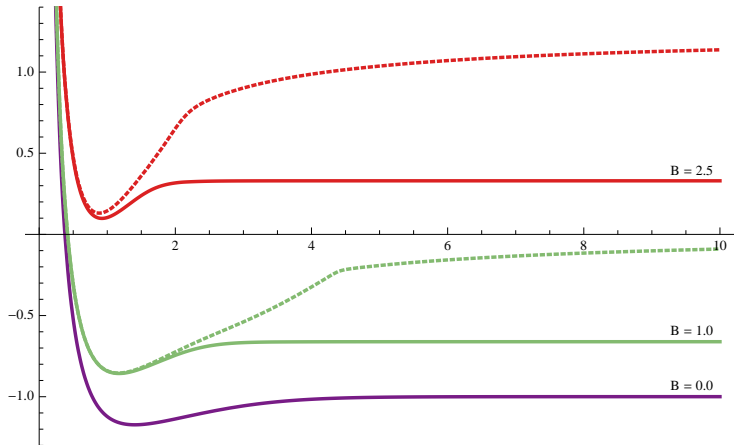
▶ Without London orbitals, the FCI method is not size extensive in magnetic fields

Section 3

Paramagnetism and diamagnetism

Paramagnetism

- Hamiltonian for a molecule in a uniform magnetic field in the z direction:

$$H = H_0 + \tfrac{1}{2}BL_z + Bs_z + \tfrac{1}{8}B^2(x^2 + y^2)$$

  - a paramagnetic, linear dependence on the magnetic field
  - a diamagnetic, quadratic dependence on the magnetic field

- The linear paramagnetic Zeeman terms are easily understood:

  - the angular momenta L_z and s_z generate a magnetic moment:

$$m_z = -\tfrac{1}{2}L_z - s_z$$

  - this magnetic moment interacts with the field B in a dipolar fashion:

$$-Bm_z = \tfrac{1}{2}BL_z + Bs_z$$

- Important consequences of the paramagnetic Zeeman terms:

  - they reduce symmetry and split energy levels
  - energy is raised or lowered, depending on orientation
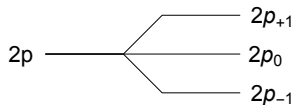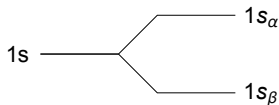
Diamagnetism

▶ Hamiltonian for a molecule in a uniform magnetic field in the z direction:

$$H = H_0 + \tfrac{1}{2}BL_z + Bs_z + \tfrac{1}{8}B^2(x^2 + y^2)$$

▶ The quadratic diamagnetic term may be understood in the following manner:

   **1** the field B induces a precession of the electrons with Larmor frequency $B/4\pi$

   2 this precession generates an induced magnetic moment proportional to the field

$$\text{charge} \times \text{frequency} \times \text{area} = -\frac{B}{4\pi}\pi(x^2 + y^2)$$

   3 this induced magnetic moment interacts with B, raising the energy quadratically

▶ Important consequences of the diamagnetic term

   1 it raises the energy of all systems

   2 it squeezes all systems

   ▶ ground-state helium atom

      ▶ transversal size $\propto 1/\sqrt{B}$

      ▶ longitudinal size $\propto 1/\log B$
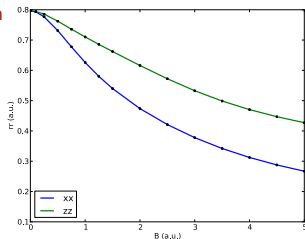
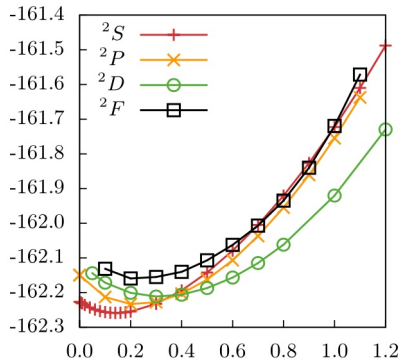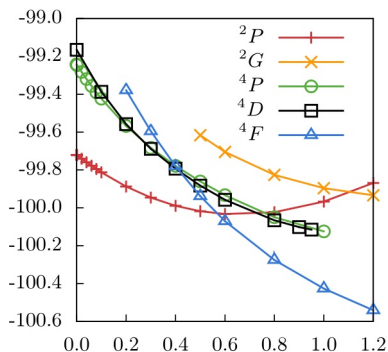# Open-shell systems – the quadratic Zeeman effect

- ▶ For open-shell atoms, we observe the quadratic Zeeman effect
  - ▶ initial energy lowering by Zeeman terms counteracted by the diamagnetic term

$$H = H_0 + Bs_z + \tfrac{1}{2}BL_z + \tfrac{1}{8}B^2\left(x^2 + y^2\right)$$

- ▶ Lowest states of the fluorine atom (left) and sodium atom (right) in a magnetic field
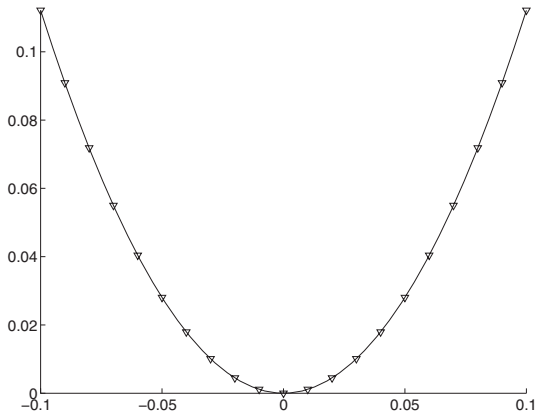

- ▶ CCSD(T) calculations in uncontracted aug-cc-pCVQZ basis (atomic units)

Closed-shell diamagnetism

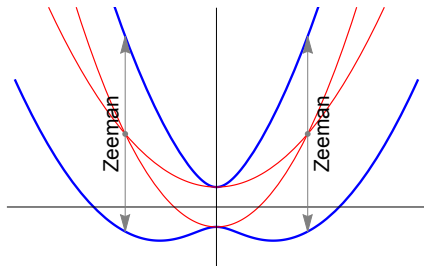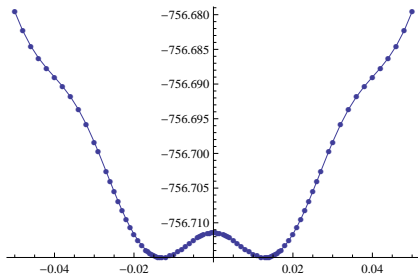▶ In a closed-shell system, ground-state energy should increase diamagnetically:

$$\langle 0|H|0\rangle = \langle 0|H_0|0\rangle + \tfrac{1}{8}B^2\langle 0|x^2 + y^2|0\rangle, \quad \langle 0|L_z|0\rangle = \langle 0|S_z|0\rangle = 0$$

▶ Energy of benzene in a perpendicular magnetic field (atomic units):

Closed-shell paramagnetism

▶ Nevertheless, closed-shell paramagnetic molecules such as C_{20} do exist

▶ Paramagnetism results from Zeeman coupling of ground and excited states in the field

  ▶ in the absence of coupling, the diamagnetic diabatic ground and excited states cross
  ▶ the Zeeman interaction generates adiabatic states with an avoided crossing
  ▶ a sufficiently strong coupling creates a double minimum (cmp. Renner–Teller)