Molecules in Magnetic Fields

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Sections

1. Electronic Hamiltonian
2. London Orbitals
3. Paramagnetism and diamagnetism
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:

$$
\begin{align*}
\dot{q} &= \frac{\partial H(q, p)}{\partial p} = \frac{p}{m} \\
\dot{p} &= -\frac{\partial H(q, p)}{\partial q} = -\frac{\partial V(q)}{\partial q}
\end{align*}
\implies m\ddot{q} = F(q) \quad \text{(Newton’s equations)}
$$

- 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
  \[ p \rightarrow -i\hbar\nabla, \quad H \rightarrow i\hbar\frac{\partial}{\partial t} \]

  - 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

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Lorentz Force and Maxwell’s Equations

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

\[
F = z \left( E + v \times B \right)
\]

- since this force depends on the velocity \( v \) of the particle, it is not conservative

- The electric and magnetic fields \( E(r, t) \) and \( B(r, t) \) satisfy Maxwell’s equations (1861–1868):

\[
\nabla \cdot E = \rho / \varepsilon_0 \quad \leftarrow \text{Coulomb’s law}
\]

\[
\nabla \times B - \varepsilon_0 \mu_0 \partial E / \partial t = \mu_0 J \quad \leftarrow \text{Ampère’s law with Maxwell’s correction}
\]

\[
\nabla \cdot B = 0
\]

\[
\nabla \times E + \partial B / \partial t = 0 \quad \leftarrow \text{Faraday’s law of induction}
\]

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

- Note:

  - when \( \rho \) and \( J \) are known, Maxwell’s equations can be solved for \( E \) and \( B \)
  - but the particles are driven by the Lorentz force, so \( \rho \) and \( J \) are functions of \( E \) and \( B \)

- 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 $B$:

$$\nabla \cdot B = 0$$

$$\nabla \times E + \frac{\partial B}{\partial t} = 0$$

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

$$\nabla \cdot B = 0 \implies B = \nabla \times A \leftarrow \text{vector potential}$$

Inserting Eq. (3) in Eq. (2) and introducing a scalar potential $\phi$, we obtain

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

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

$$E = -\nabla \phi - \frac{\partial A}{\partial t}$$

$$B = \nabla \times A$$

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

$\phi$ and $A$ are obtained by solving the inhomogeneous pair of Maxwell’s equations, containing $\rho$ and $J$. 
Gauge Transformations

Consider the following gauge transformation of the potentials:

\[
\begin{align*}
\phi' &= \phi - \frac{\partial f}{\partial t} \\
A' &= A + \nabla f
\end{align*}
\]

with \( f = f(q, t) \) ← gauge function of position and time

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

\[
\begin{align*}
E' &= -\nabla \phi' - \frac{\partial A'}{\partial t} = -\nabla \phi + \nabla \frac{\partial f}{\partial t} - \frac{\partial A}{\partial t} - \frac{\partial \nabla f}{\partial t} = E \\
B' &= \nabla \times A' = \nabla \times (A + \nabla f) = B + \nabla \times \nabla f = B
\end{align*}
\]

Conclusion: the scalar and vector potentials \( \phi \) and \( A \) 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:

\[
\nabla \cdot A' = 0 \implies \nabla \cdot (A + \nabla f) = 0 \implies \nabla^2 f = -\nabla \cdot A \leftarrow \text{Coulomb gauge}
\]

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

\[
\nabla \times A = B, \quad \nabla \cdot A = 0 \leftarrow \text{Coulomb gauge}
\]

note: \( A \) is still not uniquely determined, the following transformation being allowed:

\[
A' = A + \nabla f, \quad \nabla^2 f = 0
\]
We must construct a Hamiltonian function such that Hamilton’s equations are equivalent to Newton’s equation with the Lorentz force:

\[ \dot{q}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i} \iff ma = z(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \]

To this end, we introduce scalar and vector potentials \( \phi \) and \( \mathbf{A} \) such that

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

In terms of these potentials, the classical Hamiltonian function becomes

\[ H = \frac{\pi^2}{2m} + z\phi, \quad \pi = p - zA \quad \leftarrow \text{kinetic momentum} \]

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

\[ p \rightarrow -i\hbar\nabla, \quad H \rightarrow i\hbar \frac{\partial}{\partial t} \]

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

\[ i\hbar \frac{\partial \Psi}{\partial t} = \frac{1}{2m} \left(-i\hbar\nabla - z\mathbf{A}\right) \cdot \left(-i\hbar\nabla - z\mathbf{A}\right) \Psi + z\phi \Psi \]
Electron Spin

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

\[ H = \frac{\pi^2}{2m} - e\phi, \quad \pi = -i\hbar \nabla + eA \]

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

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

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

where \( \sigma \) contains three operators, represented by the two-by-two Pauli spin matrices

\[
\begin{align*}
\sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \\
\sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \\
\sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\end{align*}
\]

The Schrödinger equation now becomes a two-component equation:

\[
\begin{pmatrix}
\frac{\pi^2}{2m} - e\phi + \frac{e\hbar}{2m} B_z \\
\frac{e\hbar}{2m} (B_x - iB_y)
\end{pmatrix}
\begin{pmatrix}
\psi_\alpha \\
\psi_\beta
\end{pmatrix}
= E
\begin{pmatrix}
\psi_\alpha \\
\psi_\beta
\end{pmatrix}
\]

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

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

- 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 \( \sigma \) by associating an intrinsic angular momentum (spin) with the electron:

\[
s = \frac{\hbar \sigma}{2}
\]
The nonrelativistic Hamiltonian for an electron in an electromagnetic field is therefore

\[ H = \frac{\pi^2}{2m} + \frac{e}{m} B \cdot s - e\phi, \quad \pi = p + eA, \quad p = -i\hbar \nabla \]

expanding \( \pi^2 \) and assuming the Coulomb gauge \( \nabla \cdot A = 0 \), we obtain

\[
\pi^2 \psi = (p + eA) \cdot (p + eA) \psi = p^2 \psi + ep \cdot A \psi + eA \cdot p \psi + e^2 A^2 \psi
\]

\[
= p^2 \psi + e(p \cdot A) \psi + 2eA \cdot p \psi + e^2 A^2 \psi = (p^2 + 2eA \cdot p + e^2 A^2) \psi
\]

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

\[
H = \sum_i \frac{1}{2m} p_i^2 - \frac{e^2}{4\pi\epsilon_0} \sum_{K_i} \frac{Z_K}{r_{iK}} + \frac{e^2}{4\pi\epsilon_0} \sum_{i>j} r_{ij}^{-1} \quad \leftarrow \text{zero-order Hamiltonian}
\]

\[
+ \frac{e}{m} \sum_i A_i \cdot p_i + \frac{e}{m} \sum_i B_i \cdot s_i - e \sum_i \phi_i \quad \leftarrow \text{first-order Hamiltonian}
\]

\[
+ \frac{e^2}{2m} \sum_i A_i^2 \quad \leftarrow \text{second-order Hamiltonian}
\]
Magnetic Perturbations

In atomic units, the molecular Hamiltonian is given by

$$H = H_0 + \sum_i A(r_i) \cdot p_i + \sum_i B(r_i) \cdot s_i - \sum_i \phi(r_i) + \frac{1}{2} \sum_i A^2(r_i)$$

- orbital paramagnetic
- spin paramagnetic
- 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 $B$, with vector potential
  $$A_{\text{ext}}(r) = \frac{1}{2} B \times r$$
  leads to Zeeman interactions

- nuclear magnetic moments $M_K$, with vector potential
  $$A_{\text{nuc}}(r) = \alpha^2 \sum_K \frac{M_K \times r_K}{r_K^3}$$
  leads to hyperfine interactions

where $\alpha \approx 1/137$ is the fine-structure constant
Section 2

London Orbitals
Hamiltonian in a Uniform Magnetic Field

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

\[ H = H_0 + A(r) \cdot p + B(r) \cdot s + \frac{1}{2} A(r)^2 \]

- The vector potential of the uniform field \( B \) is given by:

\[ B = \nabla \times A = \text{const} \implies A_0(r) = \frac{1}{2} B \times (r - O) = \frac{1}{2} B \times r_0 \]

  - note: the gauge origin \( O \) is arbitrary!

- The orbital paramagnetic interaction becomes:

\[ A_0(r) \cdot p = \frac{1}{2} B \times (r - O) \cdot p = \frac{1}{2} B \cdot (r - O) \times p = \frac{1}{2} B \cdot L_0 \]

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

\[ L_0 = r_0 \times p \]

- The diamagnetic interaction becomes:

\[ \frac{1}{2} A_0^2 (r) = \frac{1}{8} (B \times r_0) \cdot (B \times r_0) = \frac{1}{8} \left[ B^2 r_0^2 - (B \cdot r_0)^2 \right] \]

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

\[ H = H_0 + \frac{1}{2} B \cdot L_0 + B \cdot s + \frac{1}{8} \left[ B^2 r_0^2 - (B \cdot r_0)^2 \right] \]

  - 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):
  \[ A' = A + \nabla f, \quad \phi' = \phi - \frac{\partial f}{\partial t} \]
- It can be shown that this represents a unitary transformation of \( H - i \frac{\partial}{\partial t} \):
  \[
  \left( H' - i \frac{\partial}{\partial t} \right) = \exp(-if) \left( H - i \frac{\partial}{\partial t} \right) \exp(if)
  \]
- In order that the Schrödinger equation is still satisfied
  \[
  \left( H' - i \frac{\partial}{\partial t} \right) \Psi' \iff \left( H - i \frac{\partial}{\partial t} \right) \Psi,
  \]
  the wave function undergoes a compensating unitary transformation:
  \[ \Psi' = \exp(-if) \Psi \]
- All observable properties such as the electron density are then unaffected:
  \[ \rho' = (\Psi')^* \Psi' = [\Psi \exp(-if)]^* [\exp(-if)\Psi] = \Psi^* \Psi = \rho \]
Gauge-Origin Transformations

▶ Different choices of gauge origin in the external vector potential

\[ A_0 (r) = \frac{1}{2} B \times (r - O) \]

are related by gauge transformations:

\[ A_G (r) = A_0 (r) - A_0 (G) = A_0 (r) + \nabla f, \quad f (r) = -A_0 (G) \cdot r \]

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

\[ \psi_G^{\text{exact}} = \exp [-if (r)] \psi_0^{\text{exact}} = \exp [iA_0 (G) \cdot r] \psi_0^{\text{exact}} \quad \text{(rapid) oscillations} \]

▶ Illustration: H\(_2\) on the z axis in a magnetic field \( B = 0.2 \) a.u. in the y direction

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

The exact wave function transforms in the following manner:

\[ \Psi_G^{\text{exact}} = \exp \left[ i \frac{1}{2} \mathbf{B} \times (\mathbf{G} - \mathbf{O}) \cdot \mathbf{r} \right] \Psi_0^{\text{exact}} \]

- this behaviour cannot easily be modelled by standard atomic orbitals

Let us build this behaviour directly into the atomic orbitals:

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

- \( \chi_{lm}(r_K) \) is a normal atomic orbital centred at \( \mathbf{K} \) and quantum numbers \( lm \)
- \( \omega_{lm}(r_K, \mathbf{B}, \mathbf{G}) \) 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)

Questions:
- are London orbitals needed in atoms?
- why not attach the phase factor to the total wave function instead?
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:

\[ H = H_0 + \frac{1}{2} B L_z + B s_z + \frac{1}{8} B^2 (x^2 + y^2) \]

▶ 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 \( s_z \) set up a magnetic moment:

\[ m_z = -\frac{1}{2} L_z - s_z \]

▶ this magnetic moment interacts with the field \( B \) in a dipolar fashion:

\[ -B m_z = \frac{1}{2} B L_z + B s_z \]

▶ 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:

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

- 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

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

- 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

\[
H = H_0 + B s_z + \frac{1}{2} B L_z + \frac{1}{8} B^2 \left( x^2 + y^2 \right)
\]

- 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:

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

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

![Graph showing energy as a function of magnetic field for different systems. Triangles represent finite-field calculations, and solid lines are predictions.](image-url)
Closed-shell paramagnetism

- Nevertheless, closed-shell paramagnetic molecules such as $\text{C}_{20}$ do exist

![Graph showing paramagnetic behavior](Graph)

- 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)