Molecules in Magnetic Fields

Trygve Helgaker

Hylleraas Centre, Department of Chemistry, University of Oslo, Norway
and
Centre for Advanced Study at the Norwegian Academy of Science and Letters, Oslo, Norway

European Summer School in Quantum Chemistry (ESQC) 2019
Torre Normanna, Sicily, Italy
September 8–21, 2019

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 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:

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

  - 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

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

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

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

- 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:

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

  - 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):

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

  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 $\mathbf{E}$ and $\mathbf{B}$:

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

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

  1. Eq. (1) is satisfied by introducing the vector potential $\mathbf{A}$:

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

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

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

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

$$\boxed{\begin{aligned} \mathbf{E} &= -\boldsymbol{\nabla}\phi - \frac{\partial \mathbf{A}}{\partial t} \\ \mathbf{B} &= \boldsymbol{\nabla} \times \mathbf{A} \end{aligned}}$$

- The potentials $(\phi, \mathbf{A})$ contain four rather than six components as in $(\mathbf{E}, \mathbf{B})$.
  - ϕ and $\mathbf{A}$ are obtained by solving the inhomogeneous pair of Maxwell's equations, containing ρ and $\mathbf{J}$

Gauge Transformations

- Consider the following gauge transformation of the potentials:

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

- 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:

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

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

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

  - 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:

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

- 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

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

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

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

Electron Spin

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

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

- 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

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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

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

- 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

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

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

$$\begin{aligned}\pi^2\Psi &= (\mathbf{p} + e\mathbf{A})\cdot(\mathbf{p} + e\mathbf{A})\,\Psi = p^2\Psi + e\mathbf{p}\cdot\mathbf{A}\Psi + e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi \\ &= p^2\Psi + e(\mathbf{p}\cdot\mathbf{A})\Psi + 2e\mathbf{A}\cdot\mathbf{p}\Psi + e^2A^2\Psi = \left(p^2 + 2e\mathbf{A}\cdot\mathbf{p} + e^2A^2\right)\Psi\end{aligned}$$

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

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

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

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

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

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:

$$\boxed{\mathbf{B} = \boldsymbol{\nabla} \times \mathbf{A} = \text{const} \quad \Longrightarrow \quad \mathbf{A}_\mathbf{O}(\mathbf{r}) = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) = \tfrac{1}{2}\mathbf{B} \times \mathbf{r}_\mathbf{O}}$$

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

- The orbital paramagnetic interaction becomes:

$$\mathbf{A}_\mathbf{O}(\mathbf{r}) \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) \cdot \mathbf{p} = \tfrac{1}{2}\mathbf{B} \cdot (\mathbf{r} - \mathbf{O}) \times \mathbf{p} = \tfrac{1}{2}\mathbf{B} \cdot \mathbf{L}_\mathbf{O}$$

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

$$\mathbf{L}_\mathbf{O} = \mathbf{r}_\mathbf{O} \times \mathbf{p}$$

- The diamagnetic interaction becomes:

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

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

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

  - 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

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

  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 gauge origin in the external vector potential

$$\mathbf{A}_{\mathbf{O}}(\mathbf{r}) = \tfrac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O})$$

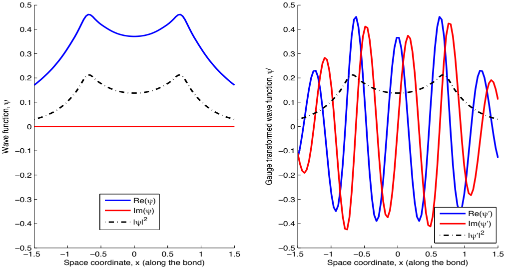
  are related by gauge transformations:

$$\mathbf{A}_{\mathbf{G}}(\mathbf{r}) = \mathbf{A}_{\mathbf{O}}(\mathbf{r}) - \mathbf{A}_{\mathbf{O}}(\mathbf{G}) = \mathbf{A}_{\mathbf{O}}(\mathbf{r}) + \boldsymbol{\nabla} f, \quad f(\mathbf{r}) = -\mathbf{A}_{\mathbf{O}}(\mathbf{G}) \cdot \mathbf{r}$$

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

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

- Illustration: H_2 on the z axis in a magnetic field $B = 0.2$ 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:

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

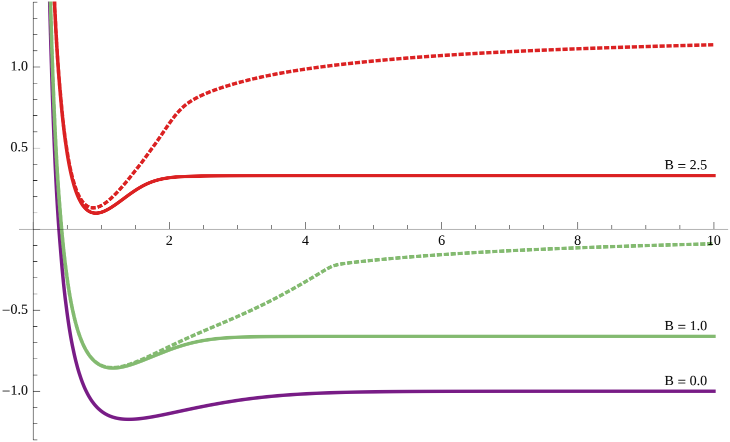
  - this behaviour cannot easily be modelled by standard atomic orbitals
- Let us build this behaviour directly into the atomic orbitals:

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

  - $\chi_{lm}(\mathbf{r}_K)$ is a normal atomic orbital centred at $\mathbf{K}$ and 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)
- 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:

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

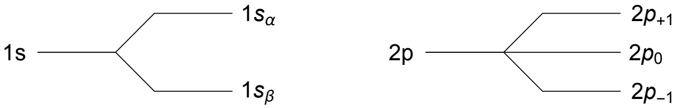
  - a paramagnetic, linear dependence on the magnetic field
  - a diamagnetic, quadratic dependence on the magnetic field
- The linear paramagnetic Zeeman terms are easily understood:
  - the angular momenta L_z and s_z set up a magnetic moment:

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

  - 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:

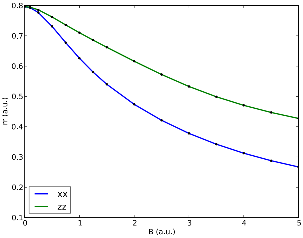
$$H = H_0 + \tfrac{1}{2} B L_z + B s_z + \tfrac{1}{8} B^2 (x^2 + y^2)$$

- 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 $\propto 1/\log B$

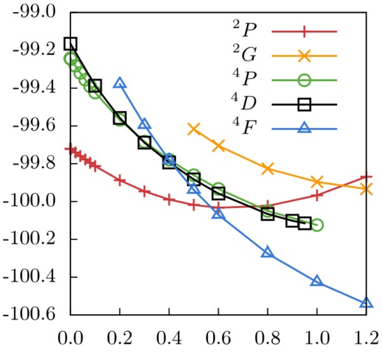


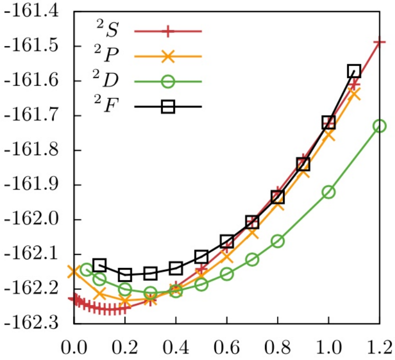
Open-shell systems – the quadratic Zeeman effect

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

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

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





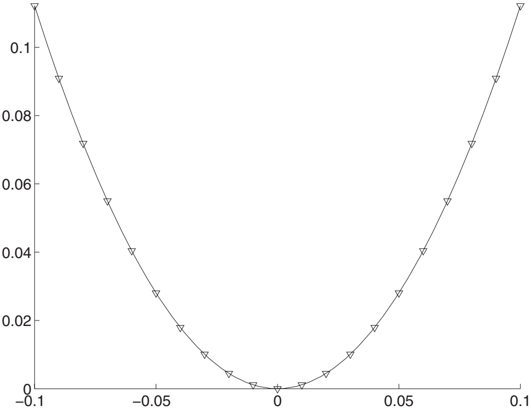
  - CCSD(T) calculations in uncontracted aug-cc-pCVQZ basis (atomic units)

Closed-shell diamagnetism

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

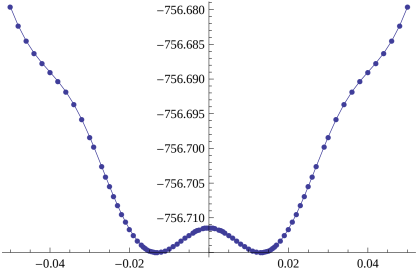
$$\langle 0|H|0\rangle = \langle 0|H_0|0\rangle + \tfrac{1}{8}B^2\langle 0|x^2+y^2|0\rangle, \quad \langle 0|L_z|0\rangle = \langle 0|S_z|0\rangle = 0$$

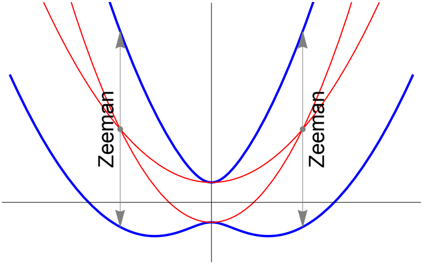
- Energy of benzene in a perpendicular magnetic field (atomic units):



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)