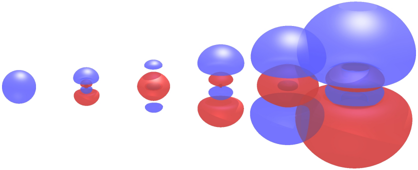


Molecular properties

Trond Saue

Laboratoire de Chimie et Physique Quantiques
CNRS/Université de Toulouse (Paul Sabatier)
118 route de Narbonne, 31062 Toulouse (FRANCE)
e-mail: trond.saue@irsamc.ups-tlse.fr

Maxwell's equations

for electric field E and magnetic field B in terms of sources ρ and j

- The homogeneous pair:

$$\begin{aligned} \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} + \partial_t \mathbf{B} &= 0; \quad \partial_t \mathbf{B} = \frac{\partial \mathbf{B}}{\partial t} \end{aligned}$$

- The inhomogeneous pair (sources):

$$\begin{aligned} \nabla \cdot \mathbf{E} &= \rho/\varepsilon_0 \\ \nabla \times \mathbf{B} - \frac{1}{c^2}\partial_t \mathbf{E} &= \mu_0 \mathbf{j} \end{aligned}$$

- Electric and magnetic constants:

$$\mu_0 \varepsilon_0 = \frac{1}{c^2}$$

- Introducing electromagnetic potentials solves the homogeneous pair

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

Maxwell's equations: The stationary case

- The homogeneous pair:

$$\begin{aligned} \boldsymbol{\nabla} \cdot \mathbf{B} &= 0 \\ \boldsymbol{\nabla} \times \mathbf{E} &= 0 \end{aligned}$$

- The inhomogeneous pair:

$$\begin{aligned} \boldsymbol{\nabla} \cdot \mathbf{E} &= \rho/\varepsilon_0 \\ \boldsymbol{\nabla} \times \mathbf{B} &= \mu_0 \mathbf{j} \end{aligned}$$

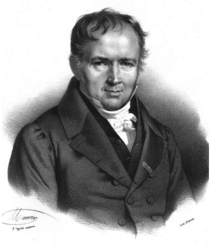
- Implies steady currents:

$$\boldsymbol{\nabla} \cdot \mathbf{j} = 0 = -\partial_t \rho$$

- A useful formula:

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{F}) = \boldsymbol{\nabla} (\boldsymbol{\nabla} \cdot \mathbf{F}) - \nabla^2 \mathbf{F}$$

$$\nabla^2\mathbf{E} = \boldsymbol{\nabla}\underbrace{(\boldsymbol{\nabla}\cdot\mathbf{E})}_{\rho/\varepsilon_0} - \boldsymbol{\nabla}\times\underbrace{(\boldsymbol{\nabla}\times\mathbf{E})}_{=0} = \boldsymbol{\nabla}\rho/\varepsilon_0$$



Siméon Denis Poisson
(1781-1840)

Each component of the electric field fulfills the Poisson equation:

$$\nabla^2\Psi(\mathbf{r}_1, t) = f(\mathbf{r}_1, t)$$

with solutions

$$\Psi(\mathbf{r}_1, t) = -\frac{1}{4\pi}\int \frac{f(\mathbf{r}_2, t)}{r_{12}} d^3\mathbf{r}_2$$

$$\mathbf{E}(\mathbf{r}_1) = -\frac{1}{4\pi\varepsilon_0}\int \frac{\boldsymbol{\nabla}_2\rho\left(\mathbf{r}_2\right)}{r_{12}}d^3\mathbf{r}_2 = \frac{1}{4\pi\varepsilon_0}\int \frac{\mathbf{r}_{12}\rho\left(\mathbf{r}_2\right)}{r_{12}^3}d^3\mathbf{r}_2$$

Charles-Augustin de Coulomb
(1736 - 1806)

Coulomb's law:

$$\begin{aligned}\mathbf{F}(\mathbf{r}_1) &= q_1\mathbf{E}(\mathbf{r}_1)\\ &= \frac{q_1}{4\pi\varepsilon_0}\int \frac{\left(\mathbf{r}_1 - \mathbf{r}'\right)\rho\left(\mathbf{r}'\right)}{\left|\mathbf{r}_1 - \mathbf{r}'\right|^3}d^3\mathbf{r}'\end{aligned}$$

Point charge:

$$\rho(\mathbf{r}') = q_2\delta\left(\mathbf{r}' - \mathbf{r}_2\right) \quad \Rightarrow \mathbf{F}(\mathbf{r}_1) = \frac{q_1 q_2\mathbf{r}_{12}}{4\pi\varepsilon_0 r_{12}^3}$$

Scalar form:

$$\mathbf{r}_{12} = r_{12}\mathbf{n}_{12} \quad \rightarrow \quad F = \frac{q_1 q_2}{4\pi\varepsilon_0 r_{12}^2}$$

Maxwell's equations: The stationary case

Magnetostatics

$$\nabla^2\mathbf{B} = \boldsymbol{\nabla}\underbrace{(\boldsymbol{\nabla}\cdot\mathbf{B})}_{=0} - \boldsymbol{\nabla}\times\underbrace{(\boldsymbol{\nabla}\times\mathbf{B})}_{\mu_0\mathbf{j}} = -\mu_0(\boldsymbol{\nabla}\times\mathbf{j})$$

Jean-Baptiste Biot

(1774-1862)

Biot-Savart law:

$$\mathbf{B}(\mathbf{r}_1) = -\frac{\mu_0}{4\pi}\int\frac{\mathbf{r}_{12}\times\mathbf{j}(\mathbf{r}_2)}{r_{12}^3}d^3\mathbf{r}_2$$

It would be tempting to insert the expression for a moving point charge

$$\mathbf{j}\left(\mathbf{r}'\right) = q_2 v_2 \delta\left(\mathbf{r}' - \mathbf{r}_2(t)\right)$$

but this is wrong, since a moving charge is not a steady current.

Hamiltonian in external fields

- From classical mechanics

$$H(\mathbf{r}, \mathbf{p}, t) = H_p(\mathbf{r}, \boldsymbol{\pi}, t) + q\phi(\mathbf{r}, t); \quad \mathbf{p} = \boldsymbol{\pi} + q\mathbf{A}$$

- Minimal substitution ($q = -e$):

$$\hat{H} \rightarrow \hat{H} - e\phi; \quad \hat{\mathbf{p}} \rightarrow \hat{\boldsymbol{\pi}} = \hat{\mathbf{p}} + e\mathbf{A}$$

- This **relativistic** coupling of particles and fields is also used in the non-relativistic domain.

Non-relativistic Hamiltonian in external fields

- Minimal substitution gives

$$h_0^{NR} = \frac{\hat{p}^2}{2m} \quad \rightarrow \quad h^{NR} = \frac{\hat{\pi}^2}{2m} - e\phi = \frac{\hat{p}^2}{2m} + \frac{e}{2m}\left[\hat{\mathbf{p}}\cdot\mathbf{A} + \mathbf{A}\cdot\hat{\mathbf{p}}\right] + \frac{e^2A^2}{2m} - e\phi$$

  - no spin interactions

- The Dirac identity

$$(\boldsymbol{\sigma}\cdot\mathbf{A})(\boldsymbol{\sigma}\cdot\mathbf{B}) = \mathbf{A}\cdot\mathbf{B} + i\boldsymbol{\sigma}\cdot(\mathbf{A}\times\mathbf{B})$$

- A special case

$$(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}}) = \hat{p}^2$$

  suggests that spin is "hidden" in the non-relativistic operator.

- Minimal substitution then gives

$$h_0^{NR} = \frac{(\boldsymbol{\sigma}\cdot\hat{\mathbf{p}})^2}{2m} \quad \rightarrow \quad h^{NR} = \frac{(\boldsymbol{\sigma}\cdot\hat{\boldsymbol{\pi}})^2}{2m} - e\phi$$

$$= \frac{\hat{p}^2}{2m} + \frac{e}{2m}\left[\hat{\mathbf{p}}\cdot\mathbf{A} + \mathbf{A}\cdot\hat{\mathbf{p}}\right] + \frac{e^2A^2}{2m} + \frac{e\hbar}{2m}(\boldsymbol{\sigma}\cdot\mathbf{B}) - e\phi$$

Relativistic Hamiltonian in external fields

- Minimal substitution gives

$$h_0^R = \beta mc^2 + c\,(\boldsymbol{\alpha}\cdot\mathbf{p}) \quad \rightarrow \quad h^R = \beta mc^2 + c\,(\boldsymbol{\alpha}\cdot\mathbf{p}) + ec\,(\boldsymbol{\alpha}\cdot\mathbf{A}) - e\phi$$

- The expectation value of the interaction Hamiltonian is given in terms of the electromagnetic potentials

$$\langle H_{int}\rangle = \int \left[\rho(\mathbf{r})\phi(\mathbf{r}) - \mathbf{j}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})\right] d^3\mathbf{r}$$

- Is it possible to express the interaction Hamiltonian directly in terms of electromagnetic fields ?
  - The answer is: Yes,
  - using **multipolar gauge**

- Scalar potential:

$$\begin{aligned}\tilde{\phi}(\mathbf{r},t) &= \tilde{\phi}(\mathbf{a},t) + \left[\left(\boldsymbol{\delta}\cdot\boldsymbol{\nabla}'\right)\tilde{\phi}\left(\mathbf{r}',t\right)\right]_{\mathbf{r}'=\mathbf{a}} + \ldots \\ &= \sum_{n=0}^{\infty}\frac{1}{n!}\left[\left(\boldsymbol{\delta}\cdot\boldsymbol{\nabla}'\right)^{n}\tilde{\phi}\left(\mathbf{r}',t\right)\right]_{\mathbf{r}'=\mathbf{a}}; \quad \boldsymbol{\delta} = \mathbf{r}-\mathbf{a}\end{aligned}$$

where **a** is the expansion point.
  - We shall set $\mathbf{a} = \mathbf{0}$, such that $\boldsymbol{\delta} = \mathbf{r}$.
- Likewise, for the vector potential

$$\tilde{\mathbf{A}}(\mathbf{r},t) = \sum_{n=0}^{\infty}\frac{1}{n!}\left[\left(\mathbf{r}\cdot\boldsymbol{\nabla}'\right)^{n}\tilde{\mathbf{A}}\left(\mathbf{r}',t\right)\right]_{\mathbf{r}'=\mathbf{0}}$$

- Using the relation $\mathbf{E} = -\boldsymbol{\nabla}\phi - \dfrac{\partial \mathbf{A}}{\partial t}$ we obtain

$$
\begin{aligned}
\widetilde{\phi}(\mathbf{r},t) &= \tilde{\phi}(\mathbf{0},t) - \textstyle\sum_{n=1}^{\infty} \frac{1}{n!}\left[(\mathbf{r}\cdot\boldsymbol{\nabla}')^{n-1}(\mathbf{r}\cdot\mathbf{E}(\mathbf{r}',t))\right]_{\mathbf{r}'=\mathbf{0}} \\
&\quad - \textstyle\frac{\partial}{\partial t}\sum_{n=1}^{\infty} \frac{1}{n!}\left[(\mathbf{r}\cdot\boldsymbol{\nabla}')^{n-1}\left(\mathbf{r}\cdot\tilde{\mathbf{A}}(\mathbf{r}',t)\right)\right]_{\mathbf{r}'=\mathbf{0}}
\end{aligned}
$$

- which can be written as a gauge transformation

$$
\widetilde{\phi}(\mathbf{r},t) = \phi(\mathbf{r},\mathbf{t}) - \frac{\partial}{\partial t}\chi(\mathbf{r},\mathbf{t})
$$

- with the gauge function

$$
\chi(\mathbf{r},t) = \sum_{n=1}^{\infty} \frac{1}{n!}\left[(\mathbf{r}\cdot\boldsymbol{\nabla}')^{n-1}\left(\mathbf{r}\cdot\tilde{\mathbf{A}}(\mathbf{r}',t)\right)\right]_{\mathbf{r}'=\mathbf{0}}
$$

- We next carry out the gauge transformation

$$\widetilde{\mathbf{A}}(\mathbf{r},t) = \mathbf{A}(\mathbf{r},\mathbf{t}) + \boldsymbol{\nabla}\chi(\mathbf{r},\mathbf{t})$$

- After some further manipulations we arrive at the final expressions

$$\begin{aligned}\phi(\mathbf{r},t) &= \tilde{\phi}(\mathbf{0},t) - \sum_{n=0}^{\infty}\tfrac{1}{(n+1)!}\left[(\mathbf{r}\cdot\boldsymbol{\nabla}')^{n}(\mathbf{r}\cdot\mathbf{E}(\mathbf{r}',t))\right]_{\mathbf{r}'=\mathbf{0}}\\ \mathbf{A}(\mathbf{r},\mathbf{t}) &= -\sum_{n=1}^{\infty}\frac{n}{(n+1)!}\left[(\mathbf{r}\cdot\boldsymbol{\nabla}')^{n-1}(\mathbf{r}\times\mathbf{B}(\mathbf{r}',t))\right]_{\mathbf{r}'=\mathbf{0}}\end{aligned}$$

- What happended to gauge freedom ?

$$\phi(\mathbf{r},t) = \phi^{[0]} - \sum_{n=0}^{\infty}\frac{1}{(n+1)!}r_{j_1}r_{j_2}\ldots r_{j_n}\left(\mathbf{r}\cdot\mathbf{E}^{[n]}_{j_1j_2\ldots j_n}\right)$$

$$\mathbf{A}(\mathbf{r},t) = - \sum_{n=0}^{\infty}\frac{n+1}{(n+2)!}r_{j_1}r_{j_2}\ldots r_{j_n}\left(\mathbf{r}\times\mathbf{B}^{[n]}_{j_1j_2\ldots j_n}\right)$$

- Uniform electric field:

$$\phi(\mathbf{r},t) = -\mathbf{r}\cdot\mathbf{E}^{[0]};\quad \mathbf{A}(\mathbf{r},t)=\mathbf{0}$$

- Uniform magnetic field:

$$\phi(\mathbf{r},t) = 0;\quad \mathbf{A}(\mathbf{r},t)=\frac{1}{2}\left(\mathbf{B}^{[0]}\times\mathbf{r}\right)$$

- For a time-dependent uniform magnetic field we get a non-uniform electric field as well

$$\mathbf{E}(\mathbf{r},t) = -\boldsymbol{\nabla}\phi - \partial_t\mathbf{A} = -\frac{1}{2}\left(\mathbf{r}\times\partial_t\mathbf{B}^{[0]}\right)$$

Multipole expansions

- In multipolar gauge the expectation value of the interaction Hamiltonian takes the form

$$\begin{aligned}\langle H_{int}\rangle &= \int [\rho(\mathbf{r})\phi(\mathbf{r}) - \mathbf{j}(\mathbf{r})\cdot\mathbf{A}(\mathbf{r})]\, d^3\mathbf{r}\\ &= Q^{[0]}\phi^{[0]} - \sum_{n=1}^{\infty}\frac{1}{n!}\mathbf{Q}^{[n]}_{j_1 j_2\ldots j_{n-1}}\cdot\mathbf{E}^{[n-1]}_{j_1\ldots j_{n-1}} - \sum_{n=1}^{\infty}\frac{1}{n!}\mathbf{m}^{[n]}_{j_1 j_2\ldots j_{n-1}}\cdot\mathbf{B}^{[n-1]}_{j_1\ldots j_{n-1}}\end{aligned}$$

- where appears electric multipoles

$$Q^{[n]}_{j_1\ldots j_n} = \int r_{j_1} r_{j_2}\ldots r_{j_n}\rho(\mathbf{r})d^3\mathbf{r}$$

- and magnetic multipoles

$$\mathbf{m}^{[n]}_{j_1\ldots j_{n-1}} = \frac{n}{n+1}\int r_{j_1} r_{j_2}\ldots r_{j_{n-1}}\,[\mathbf{r}\times\mathbf{j}(\mathbf{r})]\, d^3\mathbf{r}$$

External fields

in terms of eletromagnetic potentials

- Uniform electric field

$$\phi(\mathbf{r}_i) = -\mathbf{r}_i \cdot \mathbf{E}$$

- Uniform magnetic field

$$\mathbf{A}(\mathbf{r}_i) = \frac{1}{2}(\mathbf{B} \times \mathbf{r}_{iG})$$

- Nuclear spin:

$$\mathbf{m}_K = \gamma \mathbf{I}_K; \quad \gamma\text{ - gyromagnetic ratio}$$

- Vector potential of point-like nuclear magnetic dipole

$$\mathbf{A}_K(\mathbf{r}_i) = \frac{\mu_0}{4\pi}\frac{\mathbf{m}_K \times \mathbf{r}_{iK}}{r_{iK}^3}$$

- Corresponding magnetic field

$$\mathbf{B}_K(\mathbf{r}_i) = \boldsymbol{\nabla} \times \mathbf{A}_K = \frac{\mu_0}{4\pi}\left[\mathbf{m}_K \frac{8\pi}{3}\delta(\mathbf{r}_{iK}) - \frac{\mathbf{m}_K r_{iK}^2 - 3\mathbf{r}_{iK}(\mathbf{r}_{iK} \cdot \mathbf{m}_K)}{r_{iK}^3}\right]$$

Relativistic interaction Hamiltonians

- General form:

$$\hat{h}_{int}^{R} = ec\left(\boldsymbol{\alpha}\cdot\mathbf{A}\right) - e\phi$$

- Uniform electric field:

$$\hat{h}_{E1} = -\boldsymbol{\mu}\cdot\mathbf{E};\quad \boldsymbol{\mu} = -e\mathbf{r}$$

- Uniform magnetic field (Zeeman interaction):

$$\hat{h}_{rel}^{Z} = -\mathbf{m}_e\cdot\mathbf{B};\quad \mathbf{m}_e\left(\mathbf{r}_i\right) = \frac{1}{2}\left(\mathbf{r}_{iG}\times\hat{\mathbf{j}}_{rel}\right);\quad \hat{\mathbf{j}}_{rel} = -ec\boldsymbol{\alpha}$$

- Nuclear spins:

$$\hat{h}_{rel}^{hfs} = -\sum_{K}\mathbf{m}_K\cdot\hat{\mathbf{B}}_K^{el};\quad \hat{\mathbf{B}}_K^{el}\left(\mathbf{r}_i\right) = -\frac{\mu_0}{4\pi}\frac{\mathbf{r}_{iK}\times ec\boldsymbol{\alpha}}{r_{iK}^3}$$

Non-relativistic interaction Hamiltonian

- General form:

$$\hat{h}_{int}^{NR} = \frac{e}{2m}\left[\hat{\mathbf{p}}\cdot\mathbf{A} + \mathbf{A}\cdot\hat{\mathbf{p}}\right] + \frac{e^2A^2}{2m} + \frac{e\hbar}{2m}\left(\boldsymbol{\sigma}\cdot\mathbf{B}\right) - e\phi$$

- Coulomb gauge ($\boldsymbol{\nabla}\cdot\mathbf{A} = 0$)

$$\hat{h}_{int}^{NR} = \frac{e}{m}\left(\mathbf{A}\cdot\hat{\mathbf{p}}\right) + \frac{e^2A^2}{2m} + \frac{e}{2m}\left(\boldsymbol{\sigma}\cdot\mathbf{B}\right) - e\phi$$

- Spin interaction:

$$\hat{h} = \frac{e\hbar}{2m}\left(\boldsymbol{\sigma}\cdot\mathbf{B}\right) \quad\rightarrow\quad \frac{e}{m}\left(\hat{\mathbf{s}}\cdot\mathbf{B}\right) \quad\rightarrow\quad \frac{g_e e}{2m}\left(\hat{\mathbf{s}}\cdot\mathbf{B}\right)$$

  - Electronic g-factor

$$g_e = 2.0023193043617(15)$$

- Uniform electric field:

$$\hat{h}_{E1} = -\boldsymbol{\mu}\cdot\mathbf{E};\quad \boldsymbol{\mu} = -e\mathbf{r}$$

Non-relativistic interaction Hamiltonian

Zeeman interaction

- General form:

$$\hat{h}_{int}^{NR} = \frac{e}{m}\left(\mathbf{A}\cdot\hat{\mathbf{p}}\right) + \frac{e^2A^2}{2m} + \frac{g_e e}{2m}\left(\hat{\mathbf{s}}\cdot\mathbf{B}\right) - e\phi$$

- Uniform magnetic field (Zeeman interaction):
  - Orbital Zeeman:

$$\hat{h}^{OZ} = \frac{e}{2m}\hat{\ell}_G\cdot\mathbf{B}; \quad \hat{\ell}_G\left(i\right) = \mathbf{r}_{iG}\times\hat{\mathbf{p}}$$

  - Spin Zeeman:

$$\hat{h}^{SZ} = \frac{g_e e}{2m}\hat{\mathbf{s}}\cdot\mathbf{B}$$

  - Total paramagnetic contribution:

$$\hat{h}^{Z} = -\mathbf{m}^{para}\cdot\mathbf{B}; \quad \mathbf{m}^{para}\left(i\right) = -\frac{e}{2m}\left(\hat{\ell}_G\left(i\right) + g_e\hat{\mathbf{s}}\left(i\right)\right)$$

  - Diamagnetic contribution:

$$\hat{h}_{BB}^{dia} = \frac{e^2}{8m}\left[B^2r_{iG}^2 - \left(\mathbf{B}\cdot\mathbf{r}_{iG}\right)\left(\mathbf{r}_{iG}\cdot\mathbf{B}\right)\right]$$

Non-relativistic interaction Hamiltonian

Hyperfine interaction

- General form:

$$\hat{h}^{NR}_{int} = \frac{e}{m}\left(\mathbf{A}\cdot\hat{\mathbf{p}}\right) + \frac{e^2A^2}{2m} + \frac{g_e e}{2m}\left(\hat{\mathbf{s}}\cdot\mathbf{B}\right) - e\phi$$

- Nuclear spins:
  - Orbital contributions: $\sum_K \hat{h}^{pso}_K + \sum_{KL}\hat{h}^{dso}$
    - ★ Paramagnetic spin-orbit:

$$\hat{h}^{pso}_K = \frac{\mu_0}{4\pi}\frac{e}{mr^3_{iK}}\hat{\mathbf{m}}_K\cdot\hat{\boldsymbol{\ell}}_K$$

    - ★ Diamagnetic spin-orbit:

$$\hat{h}^{dso}_{KL} = \left(\frac{e}{2m}\right)^2\left(\frac{\mu_0}{4\pi}\right)^2\left[\frac{\left(\mathbf{m}_K\cdot\mathbf{m}_L\right)\left(\mathbf{r}_{iK}\cdot\mathbf{r}_{iL}\right)-\left(\mathbf{m}_K\cdot\mathbf{r}_{iL}\right)\left(\mathbf{r}_{iK}\cdot\mathbf{m}_L\right)}{r^3_{iK}r^3_{iL}}\right]$$

  - Spin contributions: $\sum_K\left(\hat{h}^{fc}_K + \hat{h}^{sd}_K\right)$
    - ★ Fermi contact (near-field):

$$\hat{h}^{fc}_K = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{g_e e}{2m}\right)\left(\hat{\mathbf{s}}\cdot\mathbf{m}_K\frac{8\pi}{3}\delta\left(\mathbf{r}_{iK}\right)\right)$$

    - ★ Spin-dipolar term (far-field):

$$\hat{h}^{sd}_K = -\left(\frac{\mu_0}{4\pi}\right)\left(\frac{g_e e}{2m}\right)\hat{\mathbf{s}}\cdot\left[\frac{\mathbf{m}_K r^2_{iK} - 3\mathbf{r}_{iK}\left(\mathbf{r}_{iK}\cdot\mathbf{m}_K\right)}{r^3_{iK}}\right]$$

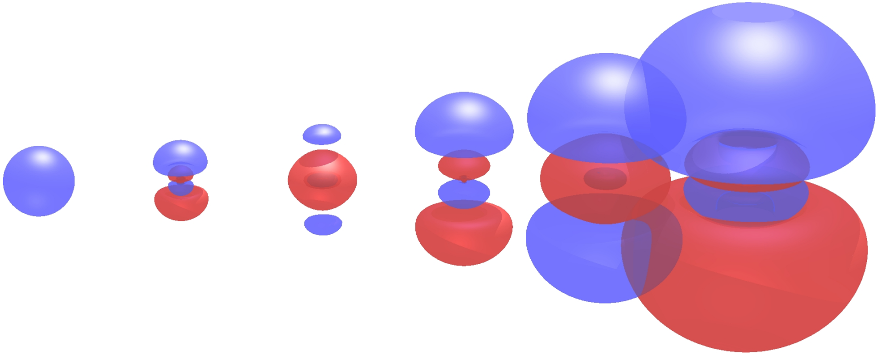
- The NMR experiment involves a external magnetic field as well as nuclear spins

$$\hat{h}_{int}^{NR} = \hat{h}^{OZ} + \hat{h}^{SZ} + \hat{h}_{BB}^{dia} \sum_K \left(\hat{h}_K^{pso} + \hat{h}_K^{fc} + \hat{h}_K^{sd} + \hat{h}_{BK}^{dia} \right) + \sum_{KL} \hat{h}^{dso},$$

- where appears the mixed diamagnetic contribution

$$\hat{h}_{BK}^{dia} = \frac{\mu_0}{4\pi} \frac{e}{2m} \left[\left[\frac{(\mathbf{B} \cdot \mathbf{m}_K)(\mathbf{r}_{iG} \cdot \mathbf{r}_{iK}) - (\mathbf{B} \cdot \mathbf{r}_{iK})(\mathbf{r}_{iG} \cdot \mathbf{m}_K)}{r_{iK}^3} \right] \right]$$

Molecular properties and response theory



- $\rho = \rho^{(0)} + \rho^{(1)} F_z + \frac{1}{2!}\rho^{(2)} F_z^2 + \frac{1}{3!}\rho^{(3)} F_z^3 + \frac{1}{4!}\rho^{(4)} F_z^4 + \frac{1}{5!}\rho^{(5)} F_z^5 + \ldots$
- $\mu_i = \int r_i \rho^{(0)} d\tau + \underbrace{\int r_i \rho^{(z)} d\tau}_{\alpha_{iz}} F_z + \frac{1}{2!} \underbrace{\int r_i \rho^{(zz)} d\tau}_{\beta_{izz}} F_z F_z + \ldots$

Response functions

- Consider a Hamiltonian on the form:

$$\hat{H} = \hat{H}_0 + \hat{V}(t); \quad \hat{V}(t) = \int_{-\infty}^{+\infty} \hat{V}(\omega) e^{-i\omega t} d\omega$$

- Hermiticity implies:

$$\hat{V}^\dagger(t) = \hat{V}(t) \quad \Rightarrow \quad \hat{V}^\dagger(\omega) = \hat{V}(-\omega)$$

- Kubo expansion:

$$\begin{aligned}
\langle\tilde{0}|\hat{\Omega}|\tilde{0}\rangle &= \langle 0|\hat{\Omega}|0\rangle \\
&+ \int_{-\infty}^{+\infty} \langle\langle \hat{\Omega}; \hat{V}(\omega)\rangle\rangle e^{-i\omega t} d\omega \\
&+ \frac{1}{2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \langle\langle \hat{\Omega}; \hat{V}(\omega_1), \hat{V}(\omega_2)\rangle\rangle e^{-i(\omega_1+\omega_2)t} d\omega_1 d\omega_2 \\
&+ \frac{1}{6}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \langle\langle \hat{\Omega}; \hat{V}(\omega_1), \hat{V}(\omega_2), \hat{V}(\omega_3)\rangle\rangle e^{-i(\omega_1+\omega_2+\omega_3)t} d\omega_1 d\omega_2 d\omega_3 \\
&+ \ldots
\end{aligned}$$

- Exact states: the connection between expectation values and energy derivatives is provided by the Hellmann-Feynman theorem.

Variational pertubation theory

- We start from an energy function

$$E \equiv E(\boldsymbol{\lambda}, \boldsymbol{\varepsilon}) \quad \begin{cases} \boldsymbol{\lambda} & \text{(variational parameters)} \\ \boldsymbol{\varepsilon} & \text{(perturbation strengths)} \end{cases}$$

- We have to carefully distinguish total and partial derivatives. Consider the differential

$$dE = \sum_X \left(\frac{\partial E}{\partial \varepsilon_X}\right) d\varepsilon_x + \sum_i \left(\frac{\partial E}{\partial \lambda_i}\right) d\lambda_i$$

- Total derivative

$$\begin{aligned} \frac{dE}{d\varepsilon_A} &= \sum_X \left(\frac{\partial E}{\partial \varepsilon_X}\right) \frac{d\varepsilon_x}{d\varepsilon_A} + \sum_i \left(\frac{\partial E}{\partial \lambda_i}\right) \frac{d\lambda_i}{d\varepsilon_A} \\ &= \frac{\partial E}{\partial \varepsilon_A} + \sum_i \left(\frac{\partial E}{\partial \lambda_i}\right) \frac{d\lambda_i}{d\varepsilon_A} \end{aligned}$$

Variational perturbation theory

- We start from

$$\left[\frac{dE}{d\varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial E}{\partial \varepsilon_A} + \sum_i \left(\frac{\partial E}{\partial \lambda_i}\right)\frac{d\lambda_i}{d\varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}}$$

- Key assumption of variational perturbation theory

$$\left.\frac{\partial E}{\partial \lambda_i}\right|_{\boldsymbol{\varepsilon}} = 0, \quad \forall \lambda_i$$

- We then get

$$\left[\frac{dE}{d\varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial E}{\partial \varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}}$$

- Second derivatives

$$\left[\frac{d^2E}{d\varepsilon_A d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial^2 E}{\partial \varepsilon_A \partial \varepsilon_B} + \sum_i \frac{\partial^2 E}{\partial \varepsilon_A \partial \lambda_i}\frac{\partial \lambda_i}{\partial \varepsilon_B}\right]_{\boldsymbol{\varepsilon}=0},$$

- ..translated to vector notation

$$\left[\frac{d^2E}{d\varepsilon_A d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = E_{AB}^{[0]} + \mathbf{E}_A^{[1]} \cdot \boldsymbol{\lambda}_B^{[1]}$$

Response equations

- The variational condition implies

$$\left.\frac{\partial E}{\partial \lambda_i}\right|_{\boldsymbol{\varepsilon}} = 0, \quad \forall \lambda_i \quad \Rightarrow \quad \frac{d}{d\varepsilon_A}\left.\frac{\partial E}{\partial \lambda_i}\right|_{\boldsymbol{\varepsilon}} = 0$$

- This allows us to generate response equations, e.g

$$\left[\frac{d}{d\varepsilon_A}\left(\frac{\partial E}{\partial \lambda_i}\right)\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial^2 E}{\partial \varepsilon_A \partial \lambda_i} + \frac{\partial^2 E}{\partial \lambda_i \partial \lambda_j}\frac{\partial \lambda_j}{\partial \varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = 0$$

- ..translated into vector notation

$$\mathbf{E}_A^{[1]} + E_0^{[2]}\boldsymbol{\lambda}_A^{[1]} = 0; \quad \Rightarrow \quad \boldsymbol{\lambda}_A^{[1]} = -\left(E_0^{[2]}\right)^{-1}\mathbf{E}_A^{[1]}$$

- Second derivative

$$\left[\frac{d^2 E}{d\varepsilon_A d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = E_{AB}^{[0]} + \mathbf{E}_A^{[1]} \cdot \boldsymbol{\lambda}_B^{[1]} = E_{AB}^{[0]} - \mathbf{E}_A^{[1]} \cdot \left(E_0^{[2]}\right)^{-1}\mathbf{E}_B^{[1]}$$

Exact-state response functions

- Let us consider the exact-state response function.
  It can be derived as a FCI problem.
- We consider a time-independent Hamiltonian on the form

$$\hat{H} = \hat{H}_0 + \hat{V}(\boldsymbol{\varepsilon}); \quad \hat{V}(\boldsymbol{\varepsilon}) = \sum_X \varepsilon_X \hat{h}_X + \frac{1}{2}\sum_{X,Y} \varepsilon_X \varepsilon_Y \hat{h}_{XY}$$

- We assume that we have the exact solutions $\{|n\rangle\}$ of $\hat{H}_0$
- We write the perturbed wave-function as

$$|\mathbf{c}\rangle = \sum_n |n\rangle c_n \quad \stackrel{\boldsymbol{\varepsilon}=\mathbf{0}}{\rightarrow} \quad |0\rangle$$

- We shall impose the normalization condition

$$\langle \mathbf{c}|\mathbf{c}\rangle = \sum_m \sum_n c_m \langle m|n\rangle c_n = \sum_n c_n^2 = 1$$

- The energy is

$$E^{FCI}(\mathbf{c}, \boldsymbol{\varepsilon}) = \langle \mathbf{c}|\hat{H}|\mathbf{c}\rangle = \sum_m \sum_n c_m \langle m|\hat{H}|n\rangle c_n \quad \stackrel{\boldsymbol{\varepsilon}=\mathbf{0}}{\rightarrow} \quad \langle 0|\hat{H}|0\rangle = E_0$$

Exact-state response functions

- We set up a Lagrangian

$$L^{FCI}(\mathbf{c}, \varepsilon, \mu) = E^{FCI}(\mathbf{c}, \varepsilon) - \mu\left(\langle \mathbf{c}|\mathbf{c}\rangle - 1\right)$$

- We impose variational conditions
  - on the CI-coefficients

$$\left.\frac{\partial L^{FCI}}{\partial c_n}\right|_{\varepsilon} = \frac{\partial E^{FCI}(\mathbf{c}, \varepsilon)}{\partial c_n} - \mu\frac{\partial\langle \mathbf{c}|\mathbf{c}\rangle}{\partial c_n} = 2\langle n|\hat{H} - \mu|\mathbf{c}\rangle = 0$$

    - ★ giving us a FCI-problem

$$H\mathbf{c} = \mu\mathbf{c}; \quad H_{mn} = \langle m|\hat{H}|n\rangle$$

  - on the Lagrange-multiplier

$$\left.\frac{\partial L^{FCI}}{\partial \mu}\right|_{\varepsilon} = 1 - \langle \mathbf{c}|\mathbf{c}\rangle = 0$$

    - ★ ..returning the normalization condition.

First-order response equations

- Since the variational conditions are to hold at *any* perturbation strength, their total derivatives with respect to perturbation strength are zero at *any* perturbation strength.
- We shall need the first-order reponse equation from the CI-coefficients:

$$
\begin{aligned}
0 = \left[\frac{d}{d\varepsilon_B}\left(\frac{\partial L^{FCI}}{\partial c_n}\right)\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} &= \left[\frac{\partial^2 L^{FCI}}{\partial c_n \partial \varepsilon_B} + \sum_m \frac{\partial^2 L^{FCI}}{\partial c_n \partial c_m}\frac{dc_m}{d\varepsilon_B} + \frac{\partial^2 L^{FCI}}{\partial c_n \partial \mu}\frac{d\mu}{d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} \\
&= \left[\langle n|\frac{\partial \hat{H}}{\partial \varepsilon_B}|\mathbf{c}\rangle + \sum_m 2\langle n|\hat{H}-\mu|m\rangle \frac{dc_m}{d\varepsilon_B} + 2\langle n|\mathbf{c}\rangle \frac{d\mu}{d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} \\
&= \langle n|\hat{h}_B|0\rangle + \sum_m 2\langle n|\hat{H}_0 - E_0|m\rangle c_m^{[B]} + 2\langle n|0\rangle \mu^{[B]} \\
&= \langle n|\hat{h}_B|0\rangle + 2\left(E_n - E_0\right) c_n^{[B]} + 2\delta_{n0}\mu^{[B]} = 0
\end{aligned}
$$

- .. as well as the Lagrange multiplier

$$
\begin{aligned}
\left[\frac{d}{d\varepsilon_B}\left(\frac{\partial L^{FCI}}{\partial \mu}\right)\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} &= \left[\underbrace{\frac{\partial^2 L^{FCI}}{\partial \mu \partial \varepsilon_B}}_{=0} + \sum_m \frac{\partial^2 L^{FCI}}{\partial \mu \partial c_m}\frac{dc_m}{d\varepsilon_B} + \underbrace{\frac{\partial^2 L^{FCI}}{\partial \mu \partial \mu}}_{=0}\frac{d\mu}{d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} \\
&= \left[-\sum_m 2\langle \mathbf{c}|m\rangle \frac{dc_m}{d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = -\sum_m 2\langle 0|m\rangle c_m^{[B]} = -2c_0^{[B]} = 0
\end{aligned}
$$

First derivative

- We first consider

$$\left.\frac{dL^{FCI}}{d\varepsilon_A}\right|_{\boldsymbol{\varepsilon}} = \left[\frac{\partial L^{FCI}}{\partial \varepsilon_A} + \sum_n \frac{\partial L^{FCI}}{\partial c_n}\frac{dc_n}{d\varepsilon_A} + \frac{\partial L^{FCI}}{\partial \mu}\frac{d\mu}{d\varepsilon_A}\right]_{\boldsymbol{\varepsilon}} = \left[\frac{\partial L^{FCI}}{\partial \varepsilon_A}\right]_{\boldsymbol{\varepsilon}},$$

  - where we used the variational conditions.

- Specifically, we calculate

$$\left.\frac{dL^{FCI}}{d\varepsilon_A}\right|_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial L^{FCI}}{\partial \varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\langle \mathbf{c}|\frac{\partial \hat{H}}{\partial \varepsilon_A}|\mathbf{c}\rangle\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \langle 0|\hat{h}_A|0\rangle$$

Second derivative

- We continue to the second derivative

$$\left.\frac{dL^{FCI}}{d\varepsilon_A d\varepsilon_B}\right|_{\varepsilon=0} = \left[\frac{d}{d\varepsilon_B}\left(\frac{\partial L^{FCI}}{\partial\varepsilon_A}\right)\right]_{\boldsymbol{\varepsilon}=\mathbf{0}}$$

$$= \left[\frac{\partial^2 L^{FCI}}{\partial\varepsilon_A\partial\varepsilon_B} + \sum_n \frac{\partial^2 L^{FCI}}{\partial\varepsilon_A\partial c_n}\frac{dc_n}{d\varepsilon_B} + \underbrace{\frac{\partial^2 L^{FCI}}{\partial\varepsilon_A\partial\mu}}_{=0}\frac{d\mu}{d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}}$$

$$= \left[\langle\mathbf{c}|\frac{\partial^2\hat{H}}{\partial\varepsilon_A\partial\varepsilon_B}|\mathbf{c}\rangle + \sum_n 2\langle\mathbf{c}|\frac{\partial\hat{H}}{\partial\varepsilon_A}|n\rangle\frac{dc_n}{d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}}$$

$$= \langle 0|\hat{h}_{AB}|0\rangle + \sum_n 2\langle 0|\hat{h}_A|n\rangle c_n^{[B]}$$

- From the response equations we know that $c_0^{[B]} = 0$ and

$$c_{n\neq 0}^{[B]} = -\frac{1}{2}\frac{\langle n|\hat{h}_B|0\rangle}{E_n - E_0} \quad\Rightarrow\quad \left.\frac{dL^{FCI}}{d\varepsilon_A d\varepsilon_B}\right|_{\varepsilon=0} = \langle 0|\hat{h}_{AB}|0\rangle - \sum_{n\neq 0}\frac{\langle 0|\hat{h}_A|n\rangle\langle n|\hat{h}_B|0\rangle}{E_n - E_0}$$

- We recover the expression from Rayleigh-Schrödinger perturbation theory
- For second-order NR magnetic properties the diamagnetic contribution is an expectation value, the paramagnetic one a linear response function.
- The linear response function contains excitation energies and transition moments.

- We write the perturbed HF state as

$$|\tilde{0}\rangle = \exp\left(-\hat{\kappa}\right)|0\rangle; \quad \hat{\kappa} = \sum_{pq} \kappa_{pq} \hat{a}_p^\dagger \hat{a}_q,$$

  where $|0\rangle$ is the unperturbed HF solution, obtained with $\hat{H}_0$.
- No Lagrange-multipliers are needed !
- The perturbed HF energy is

$$E^{HF}\left(\boldsymbol{\kappa}\right) = \langle\tilde{0}|\hat{H}|\tilde{0}\rangle = \langle 0|\exp\left(\hat{\kappa}\right)\hat{H}\exp\left(-\hat{\kappa}\right)|\tilde{0}\rangle$$

- We obtain an expansion in order of κ using the BCH-expansion

$$\begin{array}{rcll} E^{HF}\left(\boldsymbol{\kappa}\right) & = & \langle 0|\hat{H}|0\rangle & O\left(\kappa^0\right) \\ & + & \langle 0|\left[\hat{\kappa},\hat{H}\right]|0\rangle & O\left(\kappa^1\right) \\ & + & \frac{1}{2}\langle 0|\left[\hat{\kappa},\left[\hat{\kappa},\hat{H}\right]\right]|0\rangle & O\left(\kappa^2\right) \\ & + & \frac{1}{6}\langle 0|\left[\hat{\kappa},\left[\hat{\kappa},\left[\hat{\kappa},\hat{H}\right]\right]\right]|0\rangle & O\left(\kappa^3\right) \\ & + & \ldots & \end{array}$$

- Starting from

$$\hat{H}=\sum_{pq}h_{pq}\hat{a}_p^\dagger\hat{a}_q+\frac{1}{2}\sum_{pqrs}(pq|rs)\,\hat{a}_p^\dagger\hat{a}_r^\dagger\hat{a}_s\hat{a}_q$$

- .. one can derive

$$\left[\hat{\kappa},\hat{H}\right]=\hat{H}^{\{1\}}=\sum_{pq}h_{pq}^{\{1\}}\hat{a}_p^\dagger\hat{a}_q+\frac{1}{2}\sum_{pqrs}(pq|rs)^{\{1\}}\,\hat{a}_p^\dagger\hat{a}_r^\dagger\hat{a}_s\hat{a}_q,$$

- ..where

$$\begin{aligned}h_{pq}^{\{1\}} &= \sum_t(\kappa_{pt}h_{tq}-h_{pt}\kappa_{tq})\\ (pq|rs)^{\{1\}} &= \sum_t[(\kappa_{pt}\,(tq|rs)-(pt|rs)\,\kappa_{tq})+(\kappa_{rt}\,(tq|rs)-(pt|rs)\,\kappa_{ts})]\end{aligned}$$

- ..such that

$$\begin{aligned}E^{HF}(\boldsymbol{\kappa}) &= \langle 0|\hat{H}|0\rangle+\langle 0|\hat{H}^{\{1\}}|0\rangle+\frac{1}{2}\langle 0|\left[\hat{\kappa},\hat{H}^{\{1\}}\right]|0\rangle+\frac{1}{6}\langle 0|\left[\hat{\kappa},\frac{1}{2}\langle 0|\left[\hat{\kappa},\hat{H}^{\{1\}}\right]|0\rangle\right]\\ &+ \langle 0|\hat{H}|0\rangle+\langle 0|\hat{H}^{\{1\}}|0\rangle+\frac{1}{2}\langle 0|\hat{H}^{\{2\}}|0\rangle+\frac{1}{6}\langle 0|\hat{H}^{\{3\}}|0\rangle+\ldots\end{aligned}$$

- All terms of the BCH-expanded HF-energy have the same form

$$\langle 0|\hat{H}^{\{n\}}|0\rangle = \sum_i h_{ii}^{\{n\}} + \frac{1}{2}\sum_{ij}(ii||jj)^{\{n\}}; \quad (pq||rs) = \{pq|rs) - (ps|rq)$$

- We shall remove redundant variational parameters;
  they do not contribute to $\langle 0|\hat{H}^{\{1\}}|0\rangle$. We note

$$\begin{aligned}\sum_i h_{ii}^{\{1\}} &= \sum_i\sum_t(\kappa_{it}h_{ti} - h_{it}\kappa_{ti}) \\ &= \sum_i\sum_j(\kappa_{ij}h_{ji} - h_{ij}\kappa_{ji}) + \sum_i\sum_a(\kappa_{ia}h_{ai} - h_{ia}\kappa_{ai})\end{aligned}$$

- The one-electronterm involving only occupied orbitals is zero

$$\sum_i\sum_j(\kappa_{ij}h_{ji} - h_{ij}\kappa_{ji}) = \sum_i\sum_j\kappa_{ij}h_{ji} - \sum_i\sum_j h_{ij}\kappa_{ji} = \sum_i\sum_j\kappa_{ij}h_{ji} - \sum_i\sum_j h_{ji}\kappa_{ij} = 0$$

  - The same holds for the two-electron term;
    orbital rotation parameters $\{\kappa_{ij}\}$ are redundant.

- The same holds for $\{\kappa_{ab}\}$ since they do not appear in these expressions at all.
- We can therefore write

$$\hat{\kappa} = \sum_{pq}\kappa_{pq}\hat{a}_p^\dagger\hat{a}_q \quad\rightarrow\quad \hat{\kappa} = \sum_{ai}\left[\kappa_{ai}\hat{a}_a^\dagger\hat{a}_i + \kappa_{ia}\hat{a}_i^\dagger\hat{a}_a\right] = \sum_{ai}\left[\kappa_{ai}\hat{a}_a^\dagger\hat{a}_i - \kappa_{ai}^*\hat{a}_i^\dagger\hat{a}_a\right]$$

- Using the above simplifications, we first consider the HF gradient

$$E^{[1]}_{0;pq} = \left[\frac{\partial E^{HF}}{\partial \kappa_{pq}}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial}{\partial \kappa_{pq}}\langle 0|\left[\hat{\kappa},\hat{H}\right]|0\rangle\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial}{\partial \kappa_{pq}}\langle 0|\hat{H}^{\{1\}}|0\rangle\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \frac{\partial}{\partial \kappa_{pq}}\langle 0|\hat{H}^{\{1\}}_{0}|0\rangle$$

- Actual expression

$$E^{[1]}_{0;ai} = \left[\frac{\partial E^{HF}}{\partial \kappa_{ai}}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = -F_{ia}$$

- First-order properties:

$$\left[\frac{dE^{HF}}{d\varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial E^{HF}}{\partial \varepsilon_A}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \left[\frac{\partial}{\partial \varepsilon_A}\langle 0|\hat{H}|0\rangle\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \langle 0|\hat{h}_A|0\rangle$$

Hartree-Fock response theory

Second-order molecular properties

- First-order response equation
$$E_0^{[2]}\mathbf{X}_A^{[1]} = -\mathbf{E}_A^{[1]}$$
- Solution vector:
$$\mathbf{X}_A^{[1]} = \begin{bmatrix} x \\ x^* \end{bmatrix}; \quad x_{ai} = \kappa_{ai}^A$$
- Property gradient:
$$\mathbf{E}_A^{[1]} = \begin{bmatrix} g \\ g^* \end{bmatrix}; \quad g_{ai} = -h_{ia}$$
- Electronic Hessian
$$E_0^{[2]} = \begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix}; \quad \begin{aligned} A_{ai,bj} &= \left[\frac{\partial^2 E^{HF}}{\partial\kappa_{ai}^*\partial\kappa_{bj}}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = \delta_{ij}F_{ab} - \delta_{ab}F_{ji} + (ai||jb) \\ B_{ai,bj} &= \left[\frac{\partial^2 E^{HF}}{\partial\kappa_{ai}^*\partial\kappa_{bj}^*}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = (ai||bj) \end{aligned}$$
- Second-order molecular properties
$$\left[\frac{d^2 E^{HF}}{d\varepsilon_A d\varepsilon_B}\right]_{\boldsymbol{\varepsilon}=\mathbf{0}} = E_{AB}^{[0]} - \mathbf{E}_A^{[1]\dagger}\left(E_0^{[2]}\right)^{-1}\mathbf{E}_B^{[1]} = \langle 0|\hat{h}_{AB}|0\rangle + \mathbf{E}_A^{[1]}\mathbf{X}_B^{[1]}$$
- Can we somehow extract excitation energies and transition moments ?
  - Yes, we can !

- Linear response function in the static case

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle_0 = -\mathbf{E}_A^{[1]\dagger} \left(E_0^{[2]} \right)^{-1} \mathbf{E}_B^{[1]}$$

- Generalization to dynamics properties

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle_\omega = -\mathbf{E}_A^{[1]\dagger} \left(E_0^{[2]} - \omega S_0^{[2]} \right)^{-1} \mathbf{E}_B^{[1]},$$

- where appears the generalized metric

$$S_0^{[2]} = \left[\begin{array}{cc} \Sigma & \Delta \\ -\Delta^* & -\Sigma^* \end{array} \right]; \quad \begin{array}{rcl} \Sigma_{ai,bj} & = & -\delta_{ab}\delta_{ij} \\ \Delta_{ai,bj} & = & 0 \end{array}$$

Hartree-Fock response theory

Excitation energies and transition moments from the linear response function

- We start from

$$\langle\langle \hat{A}; \hat{B} \rangle\rangle_\omega = -\mathbf{E}_A^{[1]\dagger} \left(E_0^{[2]} - \omega S_0^{[2]} \right)^{-1} \mathbf{E}_B^{[1]}$$

- We insert a non-singular matrix **X**

$$\begin{aligned} \langle\langle \hat{A}; \hat{B} \rangle\rangle_\omega &= -\mathbf{E}_A^{[1]\dagger} X X^{-1} \left(E_0^{[2]} - \omega S_0^{[2]} \right)^{-1} \left(X^\dagger \right)^{-1} X^\dagger \mathbf{E}_B^{[1]} \\ &= -\mathbf{E}_A^{[1]\dagger} X \left(X^\dagger E_0^{[2]} X - \omega X^\dagger S_0^{[2]} X \right)^{-1} X^\dagger \mathbf{E}_B^{[1]} \end{aligned}$$

- The resolvent matrix $\left(X^\dagger E_0^{[2]} X - \omega X^\dagger S_0^{[2]} X \right)$ can be brought to diagonal form by solving the generalized eigenvalue problem

$$E_0^{[2]} X_n - \omega_n S_0^{[2]} X_n = 0,$$

  giving approximate exitation energies $\hbar\omega_n$.
- Corresponding approximate transition moments are obtained as $\mathbf{E}_A^{[1]\dagger} X_n$.
- Note that we obtain these quantities without explicit calculation of excited states !

More on gauge transformations

- From classical mechanics we saw that external fields are introduced into the Hamiltonian through the substitutionsFrom classical mechanics

$$H(\mathbf{r}, \mathbf{p}, t) = H_p(\mathbf{r}, \boldsymbol{\pi}, t) + q\phi(\mathbf{r}, t); \quad \mathbf{p} = \boldsymbol{\pi} + q\mathbf{A}$$

- The potentials have gauge freedom

$$\begin{aligned} \mathbf{A} \quad &\rightarrow \quad \mathbf{A}' = \mathbf{A} + \boldsymbol{\nabla}\chi \\ \phi \quad &\rightarrow \quad \phi' = \phi - \partial_t\chi \end{aligned}$$

- Similarly, in the electronic QM Hamiltonian, minimal substitution gives

$$\hat{H}(\hat{\mathbf{r}}, \hat{\mathbf{p}}, t) = \hat{H}_p(\hat{\mathbf{r}}, \hat{\boldsymbol{\pi}}, t) - e\phi(\mathbf{r}, t); \quad \hat{\mathbf{p}} = \hat{\boldsymbol{\pi}} - e\mathbf{A}$$

- Gauge transformations may be induced by **local** unitary transformations

Gauge transformation by local unitary transformation

- Suppose that we have a wave function satisfying the time-dependent wave equation

$$\left(\hat{H} - i\hbar\partial_t\right)\psi\left(\mathbf{r},t\right) = 0$$

- We consider a unitary transformation of our equation

$$\hat{U}^{-1}\left(\hat{H} - i\hbar\partial_t\right)\hat{U}\hat{U}^{-1}\psi\left(\mathbf{r},t\right) = \hat{U}^{-1}\left(\hat{H} - i\hbar\partial_t\right)\hat{U}\psi'\left(\mathbf{r},t\right) = 0$$

- We choose a local unitary transformation on the form

$$\hat{U} = \exp\left[-\frac{i}{\hbar}e\chi\left(\mathbf{r},t\right)\right]$$

- We observe the following:
    - $i\hbar\partial_t\hat{U}\psi'\left(\mathbf{r},t\right) = \hat{U}\left[e\partial_t\chi\left(\mathbf{r},t\right) + i\hbar\partial_t\right]\psi'\left(\mathbf{r},t\right)$
    - $\hat{\boldsymbol{\pi}}\hat{U}\psi'\left(\mathbf{r},t\right) = \left(-i\hbar\boldsymbol{\nabla} + e\mathbf{A}\right)\hat{U}\psi'\left(\mathbf{r},t\right) = \hat{U}\left[\hat{\boldsymbol{\pi}} - e\boldsymbol{\nabla}\chi\left(\mathbf{r},t\right)\right]\psi'\left(\mathbf{r},t\right)$

Gauge transformation by local unitary transformation

- We conclude that

$$\left(\hat{H} - i\hbar\partial_t\right)\psi(\mathbf{r},t) = \left(\hat{H}_p\left(\hat{\mathbf{r}},\hat{\boldsymbol{\pi}},t\right) - e\phi(\mathbf{r},t) - i\hbar\partial_t\right)\psi(\mathbf{r},t) = 0$$

- becomes

$$\hat{U}^{-1}\left(\hat{H} - i\hbar\partial_t\right)\hat{U}\psi'(\mathbf{r},t) = \left(\hat{H}_p\left(\hat{\mathbf{r}},\hat{\boldsymbol{\pi}}',t\right) - e\phi'(\mathbf{r},t) - i\hbar\partial_t\right)\psi'(\mathbf{r},t) = 0,$$

- with

$$\hat{\boldsymbol{\pi}}' = \hat{\mathbf{p}} + e\mathbf{A}'; \qquad \begin{array}{rcl} \mathbf{A}' & = & \mathbf{A} - \boldsymbol{\nabla}\chi \\ \phi' & = & \phi + \partial_t\chi \end{array}$$

- In principle calculated observable are invariant under the gauge transformation, e.g.

$$\langle\psi'|\hat{\Omega}|\psi'\rangle = \langle\psi|\hat{U}\hat{\Omega}\hat{U}^{-1}|\psi\rangle = \langle\psi|\hat{\Omega}|\psi\rangle,$$

<5->..but this may not be the case in a finite basis.

Looking at a gauge-transformed wave function
(Figure from Trygve Helgaker)

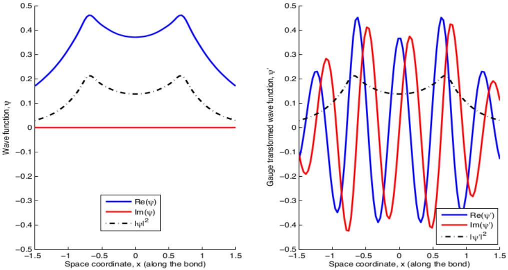
- Consider the vector potential of a uniform magnetic field

$$\mathbf{A}_O(\mathbf{r}_i) = \frac{1}{2}(\mathbf{B} \times \mathbf{r}_{iO})$$

- The gauge origin may be shifted by a gauge transformation

$$\mathbf{A}_G(\mathbf{r}_i) = \frac{1}{2}(\mathbf{B} \times \mathbf{r}_{iG}) = \mathbf{A}_O(\mathbf{r}_i) - \boldsymbol{\nabla}_i\chi(\mathbf{r}_i); \quad \chi(\mathbf{r}_i) = \mathbf{r} \cdot \mathbf{A}_O(\mathbf{G})$$

- **Illustration:** H_2 on the z-axis with a magnetic field $B = 0.2$ a.u. in the y-direction
  - wave function with a gauge origin at $O = (0, 0, 0)$ (left) and $G = (100, 0, 0)$ (right)



London orbitals

- Is there are optimal gauge origin when calculating magnetic properties ?
  - For atoms: yes
  - For molecules: no
- One option is to introduce London orbitals,
  - also called Gauge-Including Atomic Orbitals (GIAOs)

$$\chi_{\mu}\left(\mathbf{r}\right) \quad \rightarrow \quad \omega_{\mu}\left(\mathbf{r}\right) = \exp\left[-\frac{i}{\hbar}e\mathbf{r}\cdot\mathbf{A}_{G}\left(\mathbf{R}_{\mu}\right)\right]\chi_{\mu}\left(\mathbf{r}\right)$$

  - removes dependence on some arbitrary gauge origin **G** by shifting the gauge origin to the center of the basis function

Dissociation with and without London orbitals
(Figure from Trygve Helgaker)

- Let us consider the **FCI dissociation of H_2** in a magnetic field
  - full lines: with London atomic orbitals
  - dashed lines: without London orbitals