

COMPUTING ELECTRONIC SPECTRA OF MOLECULES IN STRONG MAGNETIC FIELDS USING TDHF

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Goal

To study the changes in electronic structure leading to changes in the electronic spectra when a molecule is subject to a strong magnetic field.

Methodology

1 The Electronic Hamiltonian

Non-relativistic molecular Hamiltonian in a magnetic field

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

For a uniform magnetic field in the z direction, electronic Hamiltonian is :

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

A-Vector potential , L_z – *Orbital Angular Momentum*

2 Electric Dipole Oscillator strength (f_l, f_v)

Oscillator strength f for an electric dipole transition

$$f_l = 2 \cdot \Delta E | \langle 0 | \sum_{i=1}^N r_i | X_k \rangle |^2 \quad (1)$$

$$f_v = \frac{2}{\Delta E} | \langle 0 | \sum_{i=1}^N \pi_i | X_k \rangle |^2 \quad (2)$$

where $\pi = \hat{P} + A_{tot}$, f_l – *Intensity in the length gauge*, f_v – *Intensity in the velocity gauge*

3 Linear Response Theory

The orbitals are optimized in the presence of uniform and non-uniform magnetic fields and Excitation energies and oscillator strengths are computed using the **Random Phase Approximation(RPA)**/Tamm-Dancoff approximation (**TDA or Singles-Cl**). RPA involves both excitation de exciation operators [1].

Working Equations

$$(W^{[2]} - \omega S_{\zeta\eta,\theta\kappa}^{[2]})X^{\theta\kappa} = -B_{\zeta\eta}^{[1]} \quad (3)$$

$$\hat{X} = \sum_{i=1}^m d_i \hat{b}^{(i)} + \sum_{i=1}^m d_{m+i} \hat{b}^{(i)\dagger} = \sum_{i=1}^{2m} d_i \hat{b}^{(i)} \quad (4)$$

Where

$$\begin{aligned} \omega S_{\zeta\eta,\theta\kappa}^{[2]} X^{\theta\kappa} &= \omega (S_{\eta\alpha} P^{\alpha\beta} S_{\beta\theta} X^{\theta\kappa} S_{\kappa\zeta} - S_{\eta\theta} X^{\theta\kappa} S_{\kappa\alpha} P^{\alpha\beta} S_{\beta\zeta}) \\ &= \omega S_{\zeta\alpha} [P, X]^{\alpha\beta} S_{\beta\zeta} \end{aligned} \quad (5)$$

And

$$\begin{aligned} W_{\zeta\eta,\theta\kappa}^{[2]} X^{\theta\kappa} &= -S_{\zeta\alpha} [[P, X], F(P)]^{\alpha\beta} S_{\beta\zeta} \\ &\quad - S_{\zeta\alpha} [P, G([P, X])]^{\alpha\beta} S_{\beta\zeta} \end{aligned} \quad (6)$$

Gauge Origin Invariance

- Non-relativistic molecular Hamiltonian in a magnetic field

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

- Vector potential of a uniform field, \mathbf{B} is given by:

$$\mathbf{B} = \nabla \times \mathbf{A} = \text{const} \Rightarrow \mathbf{A}_0(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times (\mathbf{r} - \mathbf{O}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}_O$$

- The **gauge origin**, \mathbf{O} , is **arbitrary** ! A change of origin is a gauge transformation. A general gauge transformation can be written as:

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

- All **observables** remain unchanged.

London

Choices of gauge origin (\mathbf{O} or \mathbf{G}) for the external vector potential are related by gauge transformations:

$$\mathbf{A}_G(\mathbf{r}) = \mathbf{A}_O(\mathbf{r}) - \mathbf{A}_O(\mathbf{G}) = \mathbf{A}_O(\mathbf{r}) + \nabla f, \quad f(\mathbf{r}) = -\mathbf{A}_O(\mathbf{G}) \cdot \mathbf{r}$$

The exact wave-function transforms accordingly as:

$$\psi_G^{exact} = e^{-if(\mathbf{r})} \psi_O^{exact} = e^{i\mathbf{A}_O(\mathbf{G}) \cdot \mathbf{r}} \psi_O^{exact} = e^{i\frac{1}{2}\mathbf{B} \times (\mathbf{G} - \mathbf{O}) \cdot \mathbf{r}} \psi_O^{exact}$$

This behaviour can be built into the atomic orbitals (AO)s. Each AO responds correctly to the applied magnetic field. This orbital Called **London** orbitals or **GIAOs** (Gauge Including AOs).

State Energy Vs B Plots

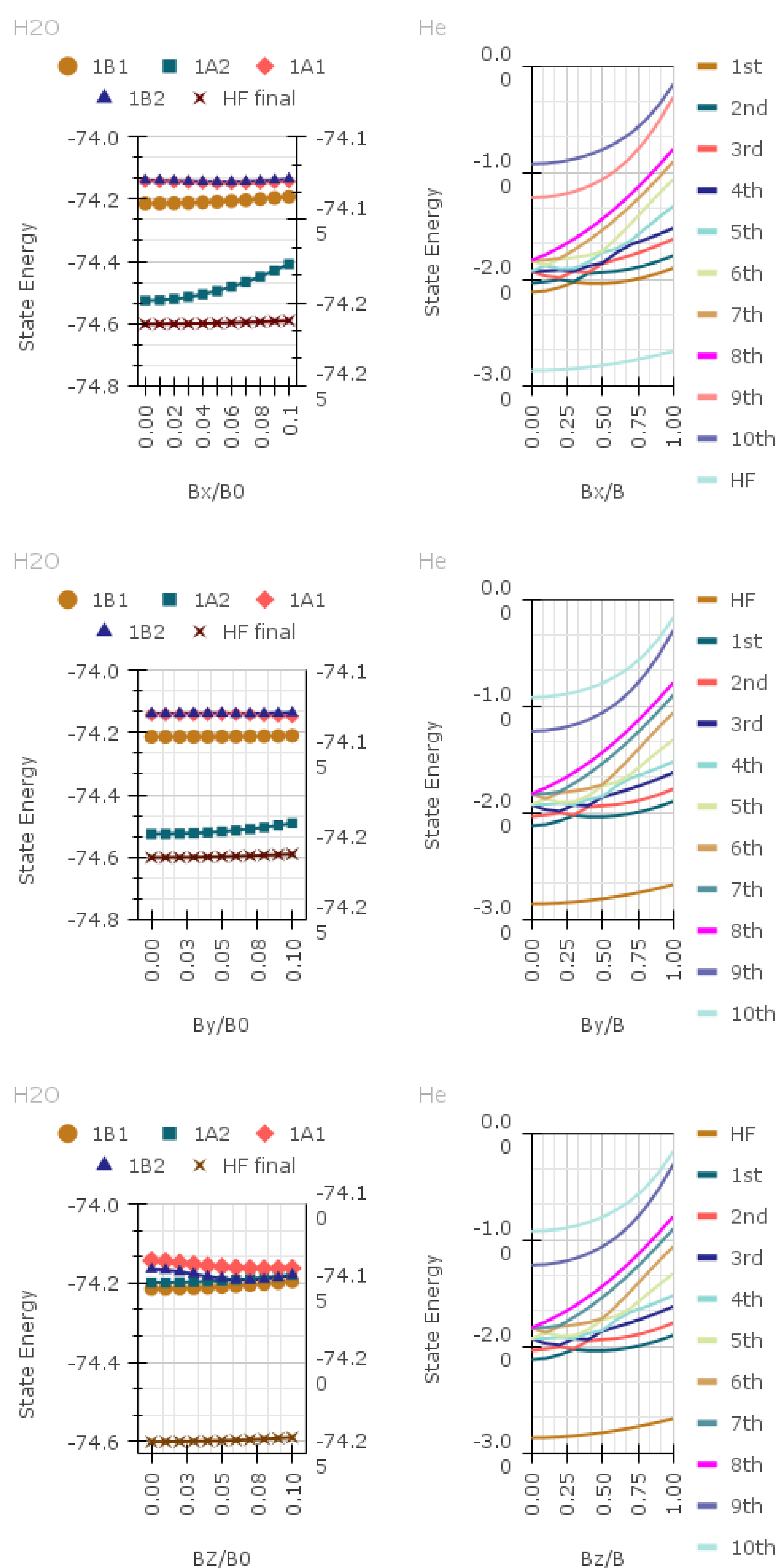


Fig. 1: Spectrum of (right)H2O placed in the yz-plane (right)Helium atom is subjected to uniform magnetic fields along the x-, y-, and z-axes. The lowest states (at zero field) are computed with GHF and the excited states with RPA using aug-cc-pVDZ basis set

Electric Dipole Oscillator strength

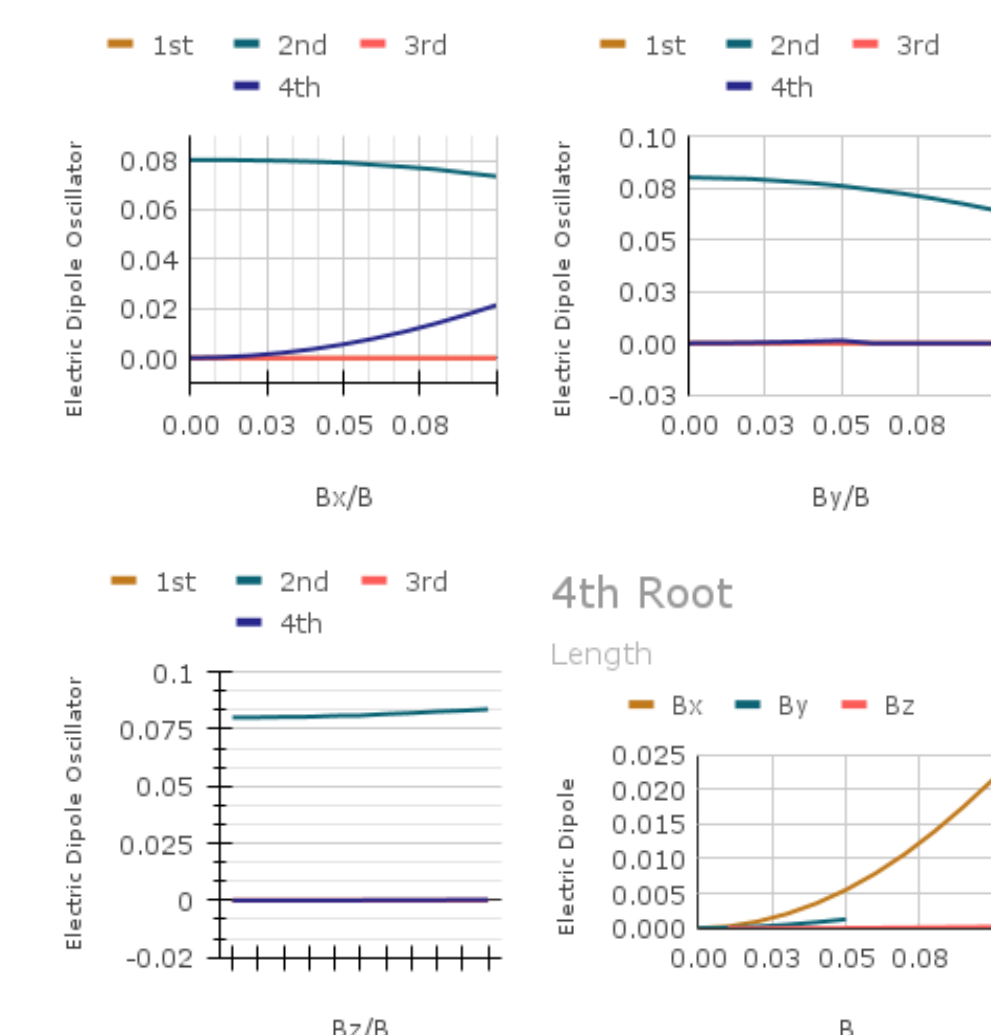


Fig. 2: Electric dipole oscillator strength of H2o Molecule subjected to uniform magnetic fields along the x-, y-, and z-axes

For larger basis set length and velocity gauges gives the same result.[1]

Density Plot

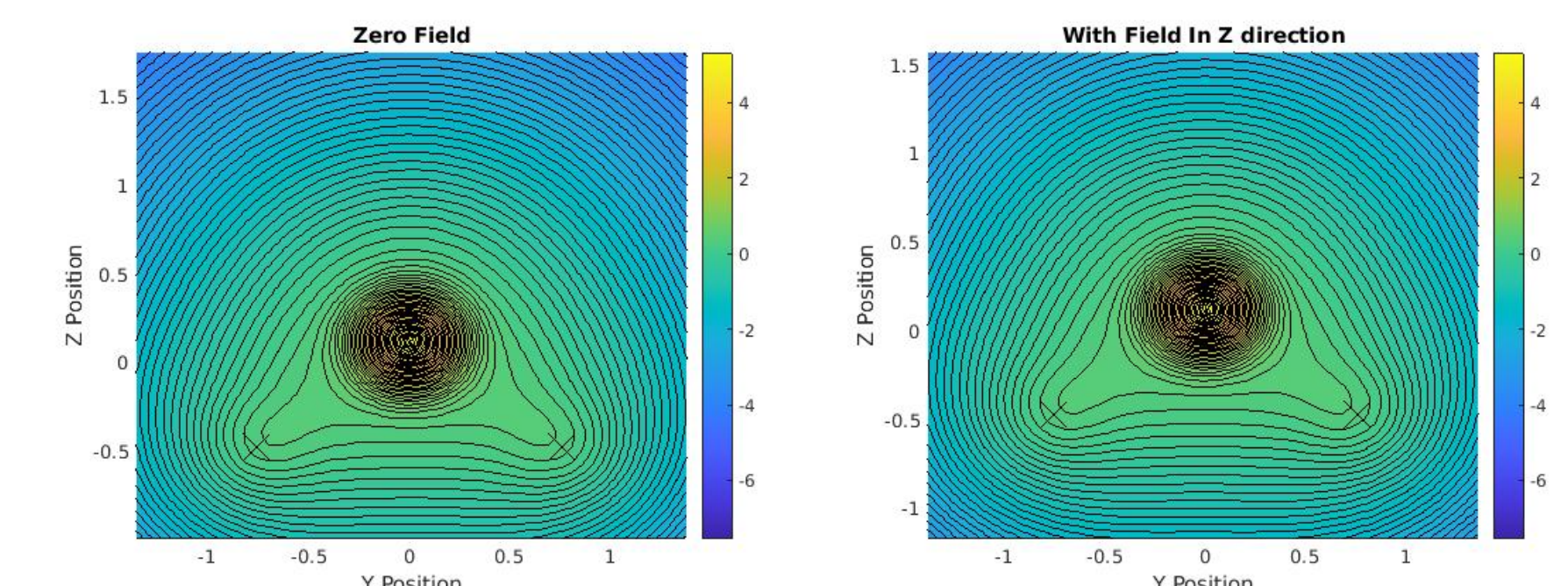


Fig. 3: Total Density in zero field(left) With field(right) under basis set aug-cc-pVDZ

Conclusions

- Strong magnetic field leads to orbital energy splitting due to lowering of symmetry
- Molecule squeezed in direction perpendicular to the field
- strong magnetic field shifts the electronic energy levels leading to change in the electronic spectra
- The electronic state which is the GS can change with changing field strength (plot will be added)

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References

- [1] Sangita Sen, Kai K Lange, and Erik I Tellgren. "Excited states of molecules in strong uniform and nonuniform magnetic fields". In: *Journal of chemical theory and computation* 15.7 (2019), pp. 3974–3990.