Ideas for set of numerical exercises

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January 11, 2023

Contents

0.1   Some links

https://kthpanor.github.io/echem/docs/intro.html https://pycrawfordprogproj.readthedocs.io/en/

1   Gaussian type orbitals (GTO)

1.1   Theory

In spherical coordinates $\chi^{GTO} = Y_{lm}(\theta, \phi)R_l^{GTO}r$, the angular part of a GTO is the usual harmonic spheric while the radial part, in spherical coordinates, is define as

$$R_l^{GTO} = N_l r^l e^{-\alpha r^2} \tag{1}$$

$$N_l = \sqrt{\frac{2^{2l+3}(l+1)!2\alpha^{l+\frac{1}{2}}}{(2l+2)!\sqrt{\pi}}} \tag{2}$$

In Cartesian coordinates, the GTO are defined as

$$\chi_{ijk}^{GTO} = N_{ijk}x^i y^j z^k e^{-\alpha(x^2+y^2+z^2)} \tag{3}$$

$$N_l = \frac{2\alpha^{\frac{3}{4}}}{\pi} \Big[\frac{(8\alpha)^{i+j+k}i!j!k!}{(2i)!(2j)!(2k)!} \Big] \tag{4}$$

where i, j and k are integer that depends on the l and m_l quantum numbers. If $i+j+k = 0$, then the orbital has spherical symmetry and is considered an s-type GTO. If $i+j+k = 1$, the GTO possesses axial symmetry along one axis and is considered a p-type GTO. When $i+j+k = 2$, there are six possible GTOs that may be constructed; this is one more than the five canonical d orbital functions for a given angular quantum number. To address this, a linear combination of two d-type GTOs can be used to reproduce a canonical d function.

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1.2 Form of the numerical exercises

- Plotting radial part of hydrogen like orbitals for different values of Z_{eff}, m, l and n quantum numbers. Example: H, He, Cl, C, O.

- Plotting radial part of Gaussian basis functions in spherical coordinates for different values of l.

- Compare both for different basis set (single, double, triple zeta) for core and valence atomic orbitals.

- Provide a function which with to compare the students answer.

- Polarization and diffuse functions: diatomic case (H_2, HCl). Plot Hartree-Fock molecular orbital for minimal basis and polarized basis. Effect on chemical bond.

1.3 To implement

- Molecular coefficients must be given (for atoms and diatomic case).

- Build-in function with normalized Gaussian.

2 Hartree Fock and molecular orbitals

2.1 Theory

- Restricted variant of Hartree-Fock and Roothan equations.

- General physical and chemical interpretation of molecular orbitals (occupied and unoccupied, Koopman's theorem, energy of Slater determinant).

2.2 Form of the numerical exercises

- Analysis and visualization of MOs for different chemical compounds: C_2H_6, C_2H_4, C_2H_2.

- Symmetry consideration (group theory).

- Plot a molecular orbital diagram.

- Link between valence orbitals, hybridization and chemical bond (single, double and triple C-C bond).

- bonding Vs non-bounding and anti-bounding orbitals.

2.3 To implement

- Visualization program within jupyter-notebook environment. Possibility: produce .molden and .spt file using PySCF and then .jpg files.

- Build-in functions for molecular orbital analysis. Print out symmetry and largest MO coefficients with corresponding AO for given threshold.

- Small HF self-made code for H_2 using given one and two electron integrals ?

3 Photoionization

3.1 Theory

The differential cross section for photoionization is given by

$$\frac{d\sigma}{d\Omega_k}[\alpha] = \frac{8\pi k E_{tot}}{c} \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} c_{klm}(\theta_k, \phi_k)[\alpha] \qquad (5)$$

where $d\Omega_k = sin(\theta_k)d\theta_k d\phi_k$, $E_{tot} = IE + E_k$ and c_{klm} is the transition probability $|\langle\phi_i| r_\alpha |\phi_e\rangle|^2$

3.2 Form of the numerical exercise

- Photoionization cross section for hydrogen-like functions: s, p, d orbitals.

- Comparison with analytical results for s.

- Photoionization cross section using GTO MOs with given LCAO coefficients and Gaussian parameters for atoms.

- Same for a molecule.

- Stress on the different approximations.

3.3 To implement

4 Chemical sensitivity in K-edge X-ray spectrum

4.1 Theory

4.2 Form of the numerical exercises

- Calculate carbon K-edge spectra of various functional groups (ex: C_2H_6, C_2H_4, C_2H_2, CH_2O, CH_2OH).

- Using HF and/or MOM excitation energy.

- Plot carbon K-edge spectra of a organic compounds containing the functional groups above.

4.3 To implement

- See the computational possibility for medium sized organic compounds.

5 Time evolution of molecular quantum state under a laser field

5.1 Theory

- Time dependent SE.

- Light as classic field.

- Matter-light interaction operator.

Possible analytical+plotting exercises:

- Steps to arrive at

$$i\hbar\frac{dc_j}{dt} = \sum_i c_i(t)\hat{V}_{ij}e^{\Delta E_{ij}t} \tag{6}$$

where $\hat{V}_{ij} = \langle \Psi_i | \hat{H}_{int} | \Psi_j \rangle$ and Ψ_i are the eigenfunctions of the unperturbed (molecular) Hamiltonian $\hat{H}_{mol}$.

- Derive 1st order expression (Dirac's variation of constants, time evolution operator method and Dyson series)

$$c_f = \frac{1}{i\hbar} \int_0^t V_{f0}(t) e^{i(\omega_f - \omega_i)t} dt \tag{7}$$

- Derive general expression for a constant perturbation $V_{ij}(t) = V_{ij}$ and for a exponentially switched on potential $V_{ij}(t) = V_{ij}(1 - e^{-kt})$. Extract physical interpretation. Final solutions:

$$|c_f|^2 = \frac{4|V_{fi}|^2}{\omega_f - \omega_i} sin^2 \left(\frac{(\omega_f - \omega_i)t}{2\hbar} \right) \tag{8}$$

$$|c_f|^2 = \frac{|V|^2 p_2(t)}{\omega_{21}^2} \quad p_2(t) \text{ is a function of } \frac{k}{\omega_{21}} \text{ and t} \tag{9}$$

- Derive general expression for an oscillating potential (harmonic perturbation). Extract physical interpretation. Final solutions:

$$|c_f|^2 = \frac{4|V_{fi}|^2}{(\omega_i - \omega_f)} sin^2 \frac{1}{2}(\omega_f - \omega_i - \omega_{field}) \tag{10}$$

- The long wavelength approximation: multipole expansion of the plane wave and the dipole approximation.

- Laser pulse shape. Link to pump probe experiment

5.2 Form of the numerical exercises

- Build set of excited Slater determinant: Slater-states. With related tdm.

- Solve full TDSE within the electronic Slater states basis for different Laser pulse shape.

- Plot and discuss the results.

5.3   To implement

- Verify code (energy of Slater determinant)

- implement MOM calculation ? Reduce number of determinant: some valence excitation and core excitation only ? Tdm in MOM ?

- Same exercise within vibrational basis ?

6   Post Hartre-Fock approaches