Computing Excited States properties of molecule under Non-uniform Magnetic Fields: Nonperturbative Approach

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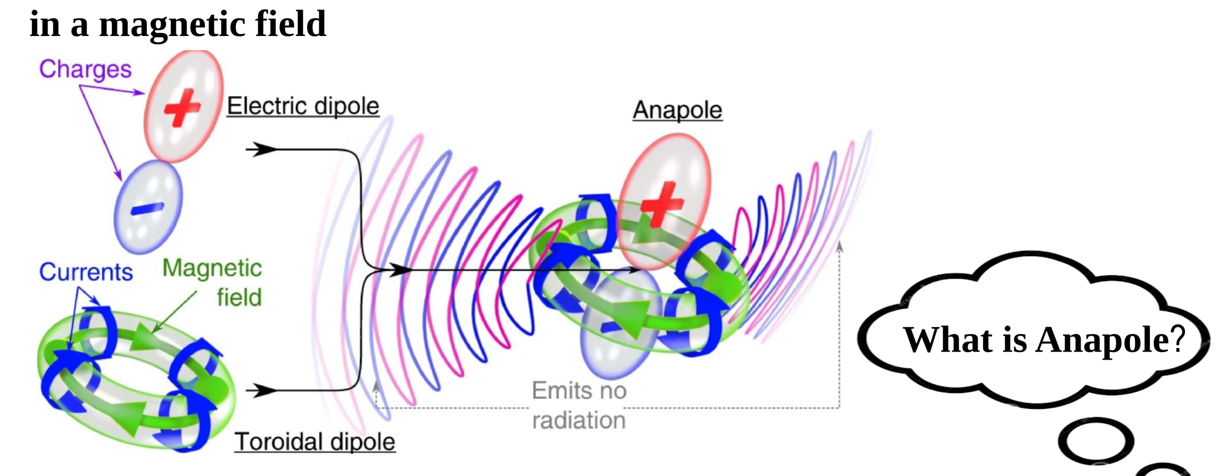
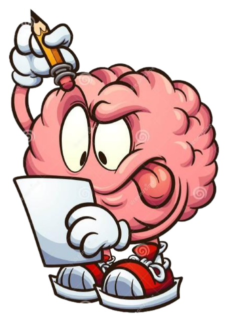
1. Objective

- ❖ Computing the Electronic Anapole Susceptibility Comparison between Ground State and Lowest Excited State
- ❖ Quantity to measure the response of the electronic state to non-uniformities in a magnetic field





- ❖ Anapole moments are those moments which couple linearly to the curl of the magnetic field
- ❖ Permanent electronic anapole moments:
  - ➢ Toroidal shape(Fullerene)
  - ➢ Lack of improper rotation symmetry(chiral radical)

2. Molecular Hamiltonian and Properties

$$\hat{H}=\frac{1}{2}\sum_l \widehat{\pi_l^2}-\sum_l v(r_l)+\sum_{k>l}\frac{1}{r_{kl}}+\sum_l B_{tot}(r_l).\hat{S_l}$$

$$A_{tot}(r)=\frac{1}{2}\mathrm{B}\times(r-g)-\frac{1}{3}(\mathrm{r-h})\times((r-h)^T b)$$

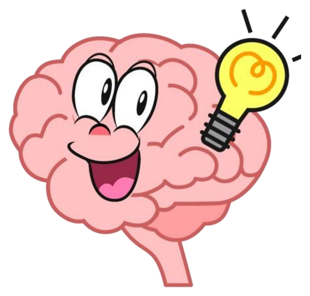
Linearly Varying nonuniform magnetic field

$$B_{tot}(\mathrm{r})=\nabla\times A_{tot}(r)=\mathrm{B}+(r-h)^T\mathrm{b}-\frac{1}{3}(\mathrm{r-h})T_r(b)$$

In our calculation

$$\nabla\cdot B_{(tot)}=0 \qquad \mathrm{b}=b^T$$

$$\nabla\times B_{(tot)}=\mathrm{C} \qquad C_\alpha=\epsilon_{\alpha\beta\gamma}\, b_{\beta\gamma}$$



3. Molecular Hamiltonian and Properties Cont….

In a non-perturbative setting, the energy E as well as expectation value properties can be obtained directly as functions of B and C

$$E(B,\mathbb{C})\approx E_0+B\cdot J_G-\frac{1}{2}\mathbb{C}\cdot\mathrm{a}-\frac{1}{2}B^T\chi B-B\mathcal{M}\mathbb{C}-\frac{1}{2}\mathbb{C}^T\mathcal{A}\mathcal{C}$$

Turning to the second-order susceptibilities, the defining expressions are Specifically $\mathcal{A}$ denotes the anapole susceptibility tensor

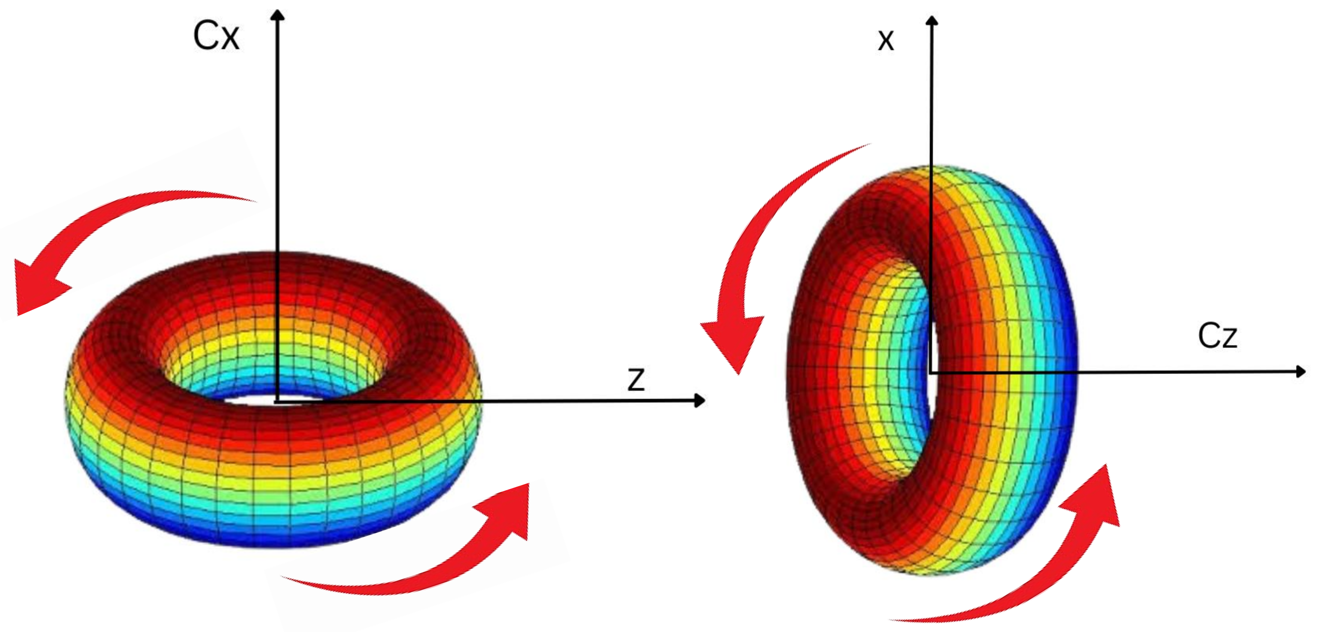
$$\mathcal{A}'_{\alpha\beta}=-2\frac{\partial^2 E\,(\mathrm{B},\mathbb{C})}{\partial\mathbb{C}_\alpha\partial\mathbb{C}_\beta}\,|\,B_{=0}\mathbb{C}_{=0}$$

General HF Model with an external non-uniform magnetic field

$$\phi_K(r)=\sum_a C^{a,K\uparrow}\chi_a(r)\binom{1}{0}+\sum_a C^{a,K\downarrow}\chi_a(r)\binom{0}{1}$$
$$=\sum_a\chi_a(r)\binom{C^{a,K\uparrow}}{C^{a,K\downarrow}}$$

$$D^{2\times2}(\mathrm{r},r')=\sum_K^{OCC}\phi_K(r)\phi_K(r')^\dagger$$
$$=\sum_{ab}\chi_a(r)\begin{pmatrix}D^{\uparrow\uparrow;ab} & D^{\uparrow\downarrow;ab}\\ D^{\downarrow\uparrow;ab} & D^{\downarrow\downarrow;ab}\end{pmatrix}\chi_b(r')^*$$

4. Anapole Moment

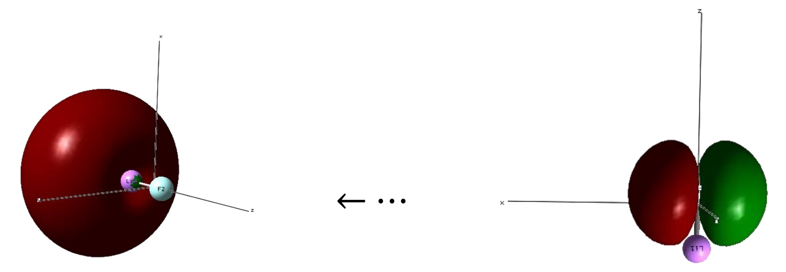


When a Magnetic field with Curl C is applied , Meridional electric currents like those on a toroidal charge distribution are induced. These generate an induce Anapole moment

5. Symmetry Effect

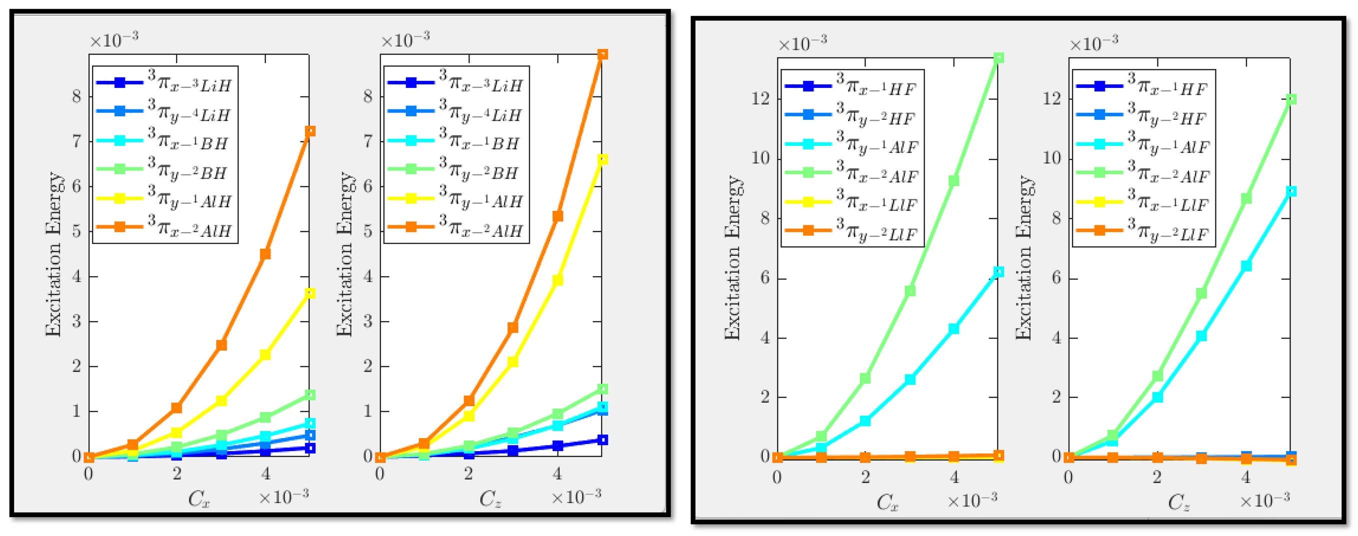
Electronic Transitions in different symmetries

Molecule	1st Symmetry	2nd Symmetry	3rd Symmetry	4th Symmetry
LiH	$^3\Sigma_z$	$^1\Sigma_x$	$^3\Pi_x$	$^3\Pi_y$
BH	$^3\Pi_x$	$^3\Pi_y$	$^1\Pi_y$	$^1\Pi_x$
AlH	$^3\Pi_y$	$^3\Pi_x$	$^1\Pi_x$	$^1\Pi_y$
LiF	$^3\Pi_x$	$^3\Pi_y$	$^1\Pi_x$	$^1\Pi_y$
HF	$^3\Pi_x$	$^3\Pi_y$	$^1\Pi_x$	$^1\Pi_y$
AlF	$^3\Pi_y$	$^3\Pi_x$	$^1\Pi_y$	$^1\Pi_x$



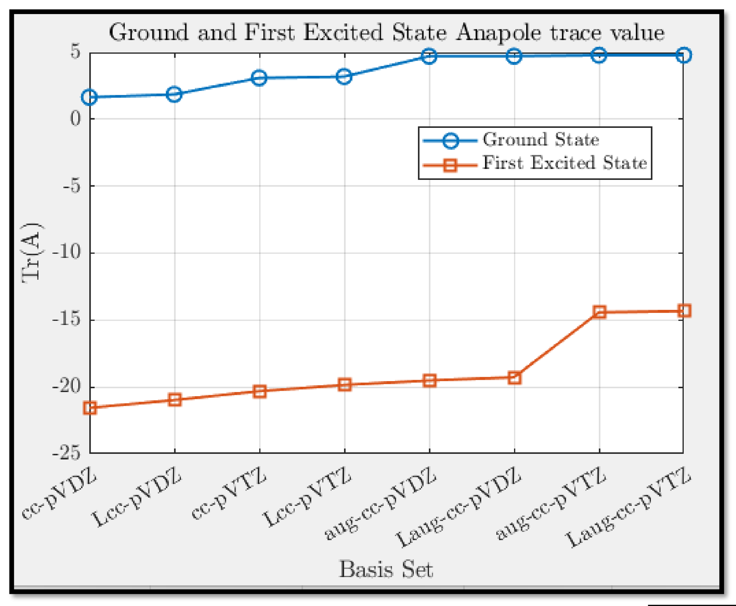
Representation of First Excited electronic transition in LiF Molecule

6. Anapole susceptibility



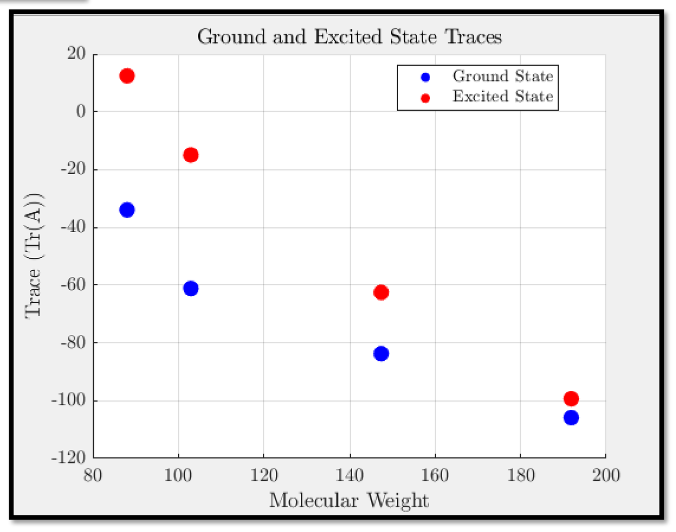
- ❖ In hetero diatomic $\Sigma\rightarrow\pi$ excitation show low sensitivity toward C in non uniform magnetic field ,HF,LiF,AlF singlet and triplet pi state compared to hydride molecules this is in spite of the fact X-F bonds are longer than X-H bonds. This likely due to the high electronegativity of fluorine atom, which binds the π electron very strongly
- ❖ Cz destroyed the nodal plane of p orbital resulting in the larger response in the Cz when compared with the response to Cx. this is true for hydrides vice versa for fluoride

7. Anapole susceptibility Cont….



- ❖ Excited electronic state is more sensitive than ground state to non-uniform magnetic field

Representation of size effect of orbital anapole moment to chirality



8. Conclusions & Future outlook

- ❖ Excited-state anapole susceptibility is interesting because it delves into the quantum nature of electromagnetic interactions, contributes to our understanding of fundamental physics, and has potential applications in various scientific and technological domains.
- ❖ Due to more varied and loosely bound electronic densities, the excited state shows a larger response to external perturbations.
- ❖ Greater spin densities can be induced for :
  - ➢ Less symmetric electronic states
  - ➢ Larger atoms trends $\mathcal{A}$ are somewhat similar to that for electronic polarizability χ

- ❖ Plan able to analyze the joint influences of orbital and spin on the energies and anapole susceptibilities of various molecules.
- ❖ Study the factors influencing objects like induced anapole moments

9. Reference & Acknowledgements

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2.Tellgren, E. I., and Fliegl, H. "Non-perturbative treatment of molecules in linear magnetic fields: Calculation of anapole susceptibilities," *The Journal of Chemical Physics*, V. 139, No. 16, 2013.

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Thank You!

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