PDM Calculation of Molecule using Finite Field

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1 Introduction

The permanent dipole moment of a molecule is a fundamental property that describes the separation of positive and negative charges. The finite field method offers a numerical technique to estimate by observing the variation of the molecular energy in response to an external electric field.

2 Perturbative Finite Field Method

When an external electric field $\vec{E}$ is applied along the z-direction, the Hamiltonian of the molecular system is perturbed as:

$$\hat{H} = \hat{H}_0 + \lambda \hat{O}, \tag{1}$$

where $\hat{H}_0$ is the unperturbed molecular Hamiltonian and $\hat{O}$ is the dipole moment operator in the z-direction and λ is the perturbation strength.
From first-order perturbation theory, the energy correction due to the field is given by:

$$E(\lambda) = E_0 + \lambda \langle \Psi_0 | \hat{O} | \Psi_0 \rangle , \tag{2}$$

where E_0 is the unperturbed energy and Ψ_0 is the unperturbed wavefunction.
Thus, the dipole moment in the z-direction can be obtained as:

$$\langle \hat{O} \rangle = \left| \frac{\partial E}{\partial \lambda} \right|_{\lambda \to 0} \tag{3}$$

Instead of computing the derivative analytically, we approximate it numerically using the central difference formula:

$$\langle \hat{O} \rangle \approx \lim_{\lambda \to 0} \frac{E(+\lambda) - E(-\lambda)}{2\lambda} \tag{4}$$

A small perturbative field (typically on the order of 10^{-4} to 10^{-3} a.u.) is applied along the z-axis, and the total energy is computed for both positive and negative field values. We will get the both values of $E(\lambda)$ using Quantum annealling eignsolver.

3 Background

The electronic Schrödinger equation can be expressed as:

$$\hat{H} | \Psi \rangle = E | \Psi \rangle , \tag{5}$$

where $\hat{H}$ is the Hamiltonian operator, $|\Psi\rangle$ is the exact electronic wavefunction, and E is the electronic energy.

In CI methods, the wavefunction $|\Psi\rangle$ is expanded as a linear combination of Slater determinants:

$$|\Psi\rangle = \sum_i c_i \, |\Phi_i\rangle \, , \tag{6}$$

where $|\Phi_i\rangle$ are the determinants and c_i are the expansion coefficients.

4 Wavefunction Representation

The electronic wavefunction is expressed as:

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{n=1} c_n|\Phi_n\rangle, \tag{7}$$

where:

- $|\Phi_0\rangle$: Hartree-Fock (HF) determinant.
- $|\Phi_n\rangle$: Electronically excited determinants from HF.
- c_0, c_n: Coefficients representing contributions for respective state.

5 Hamiltonian Formulation

The second-quantized Hamiltonian is:

$$H = \sum_{pq} h_{pq} a_p^\dagger a_q + \frac{1}{2} \sum_{pqrs} h_{pqrs} a_p^\dagger a_q^\dagger a_s a_r \tag{8}$$

where:

- h_{pq}: One-electron integrals.
- h_{pqrs}: Two-electron integrals.
- $a_p^\dagger, a_q$: Creation and annihilation operators.

6 Energy Calculation

We have used SrF molecule with reduce active space 23, 24, 25, 26 having specification as:

- Number of orbitals: 8
- Number of electrons: 3
- Number of up spin electrons: 2
- Number of down spin electrons: 1
- Number of states with higher excitation : 24
- Number of states with lower SD : 22

6.1 From DIRAC 22 :

1 D = 0.3934 a.u.
Nuclear dipole moment = 35.290635377386 a.u.
Total CCSD energy($\lambda = 0$): -3241.560827750358385
Total CCSD energy($\lambda = -0.001$):-3241.596815215792049
Total CCSD energy($\lambda = +0.001$):-3241.524873497649423

6.1.1 Backwards Finite Difference $CCSD$:

$$EDM = \left| \frac{E(+\lambda) - E(0)}{\lambda} \right|$$
$$= \frac{3241.596815215792049 - 3241.560827750358385}{0.001} = 35.987465433664$$

Total PDM in a.u. = 35.987465433664 a.u. - 35.290635377386 a.u. = 0.696830056278 a.u.
Total PDM in debye = 0.696830056278/0.3934 = 1.7713016173817 D

6.1.2 Forwards Finite Difference $CCSD$:

$$EDM = \left| \frac{E(0) - E(-\lambda)}{\lambda} \right|$$
$$= \frac{3241.560827750358385 - 3241.524873497649423}{0.001} = 35.954252708962$$

Total PDM in a.u. = 35.954252708962 a.u. - 35.290635377386 a.u. = 0.663617331576 a.u.
Total PDM in debye = 0.663617331576/0.3934 = 1.6868767960753 D

6.2 Midpoint Finite Difference $CCSD$:

$$EDM = \left| \frac{E(+\lambda) - E(-\lambda)}{2\lambda} \right|$$
$$= \frac{3241.596815215792049 - 3241.524873497649423}{2 * 0.001} = 35.970859071313$$

Total PDM in a.u. = 35.970859071313 a.u. - 35.290635377386 a.u. = 0.680223693927 a.u.
Total PDM in debye = 0.680223693927/0.3934 = 1.72908920672852 D

6.3 From FCI and SA:

6.3.1 Before adding Nuclear repulsion term:

Energy calculation for zero pertubation :
Ground state energy from SA: -1.90096767
Ground state energy FCI: -1.88887208
Minimum error percentage: 0.640361%

After applying the perturbation -0.001:
Ground state energy from SA: -1.90179514
Ground state energy FCI: -1.89124202
Minimum error percentage: 0.557999%

After applying the perturbation +0.001
Ground state energy from SA: -1.89067440
Ground state energy FCI: -1.88660713
Minimum error percentage: 0.215586%

6.3.2 After adding Nuclear repulsion term:

Without perturbation:
Ground state energy from SA: -3241.57505095
Ground state energy FCI: -3241.56295535
Minimum error percentage: 0.000373%

After applying the perturbation -0.001:
Ground state energy from SA: -3241.60932570
Ground state energy FCI: -3241.59877259
Minimum error percentage: 0.000326%

After applying the perturbation +0.001:
Ground state energy from SA: -3241.53124943
Ground state energy FCI: -3241.52718217
Minimum error percentage: 0.000125%

6.3.3 Forwards Finite Difference FCI:

$$EDM = \left|\frac{E(+\lambda) - E(0)}{\lambda}\right|$$
$$= \frac{3241.56295535 - 3241.52718217}{0.001} = 35.77317318$$

Total PDM in a.u. = 35.77317318 a.u. - 35.290635377386 a.u. = 0.482537802614 a.u.
Total PDM in debye = 0.482537802614 * 2.54158 = 1.225 D

6.3.4 Backwards Finite Difference FCI:

$$EDM = \left|\frac{E(0) - E(-\lambda)}{\lambda}\right|$$
$$= \frac{3241.59877259 - 3241.56295535}{0.001} = 35.81624$$

Total PDM in a.u. = 35.81624 a.u. - 35.290635377386 a.u. = 0.525604622614 a.u.
Total PDM in debye = 0.525604622614* 2.54158 = 1.335 D

6.3.5 Midpoint Finite Difference FCI:

$$EDM = \left|\frac{E(+\lambda) - E(-\lambda)}{2\lambda}\right|$$
$$= \frac{3241.59877259 - 3241.52718217}{2 * 0.001} = 35.535295$$

Total PDM in a.u. = 35.535295 a.u. - 35.290635377386 a.u. = 0.244659622614 a.u.
Total PDM in debye = 0.244659622614 * 2.54158 = 0.621 D

6.3.6 Forward Finite Difference SA:

$$EDM = \left|\frac{E(+\lambda) - E(0)}{\lambda}\right|$$
$$= \frac{3241.57505095 - 3241.53124943}{0.001} = 43.80152$$

Total PDM in a.u. = 43.80152 a.u. - 35.290635377386 a.u. = 8.510884622614 a.u.
Total PDM in debye = 8.510884622614 * 2.54158 = 21.64 D

6.3.7 Backward Finite Difference SA:

$$EDM = \left| \frac{E(0) - E(-\lambda)}{\lambda} \right|$$
$$= \frac{3241.60932570 - 3241.57505095}{0.001} = 34.27475$$

Total PDM in a.u. = 34.27475 a.u. - 35.290635377386 a.u. = -1.015885377386 a.u.
Total PDM in debye = 1.015885377386* 2.54158 = -2.58 D

6.3.8 Midpoint Finite Difference SA:

$$EDM = \left| \frac{E(+\lambda) - E(-\lambda)}{2\lambda} \right|$$
$$= \frac{3241.60932570 - 3241.53124943}{2 * 0.001} = 39.038135$$

Total PDM in a.u. = 39.038135 a.u. - 35.290635377386 a.u. = 3.747499622614 a.u.
Total PDM in debye = 3.747499622614* 2.54158 = 9.52 D

References