

## Abstract

In UV/Vis and IR spectroscopies, the dipole moments, the transition dipole moments and oscillator strengths are valuable quantities that provide a better understanding of the underlying excitation processes. However, from a computational point of view, obtaining accurate values for such one-electron properties is very challenging. The usual way to benchmark these properties is to rely on linear-response (LR) or equation-of-motion (EOM) coupled-cluster (CC) calculations. However, it is difficult to reliably assess the accuracy of these methods, especially at low orders. In the present poster, we investigate the range of applicability of a selected configuration interaction (SCI) method known as “*Configuration Interaction using a Perturbative Selection made Iteratively*” (CIPSI) [1] for the computation of near full CI (FCI) quality ground- and excited-state dipole moments and oscillator strengths. The CIPSI algorithm is implemented in the open-source software **QUANTUM PACKAGE** [2], freely accessible on Github at <https://quantumpackage.github.io/qp2/>.

## Dipole moments via expectation values

The dipole moment associated with the electronic state  $\Psi_k$  is

$$\mu_k = - \sum_i \langle \Psi_k | \mathbf{r}_i | \Psi_k \rangle + \sum_A Z_A \mathbf{R}_A, \quad (1)$$

where  $\mathbf{r}_i$  and  $\mathbf{R}_A$  are respectively the coordinates of the  $i$ th electron and the  $A$ th nucleus of charge  $Z_A$ .

## Oscillator strengths

The oscillator strength between two electronic states  $k$  and  $l$  can be computed in different gauges, but they are only equals for the exact wave function [3]. The different gauges are the **length**, **velocity**, and **mixed**:

$$f_{kl}^L = \frac{2\Delta E_{kl}}{3} \lambda_{kl} \lambda_{lk}, \quad f_{kl}^V = \frac{2}{3\Delta E_{kl}} \nu_{kl} \nu_{lk}, \quad f_{kl}^{LV} = -\frac{2i}{3} \lambda_{kl} \nu_{lk}, \quad (2)$$

where  $\Delta E_{kl}$  is the difference between the variational energies of the states  $\Psi_k$  and  $\Psi_l$ ,

$$\lambda_{kl} = - \sum_i \langle \Psi_k | \mathbf{r}_i | \Psi_l \rangle, \quad \nu_{kl} = - \sum_i \langle \Psi_k | \mathbf{p}_i | \Psi_l \rangle, \quad (3)$$

and  $\mathbf{p}_i$  is the momentum operator of electron  $i$ .

## Basis set dependency

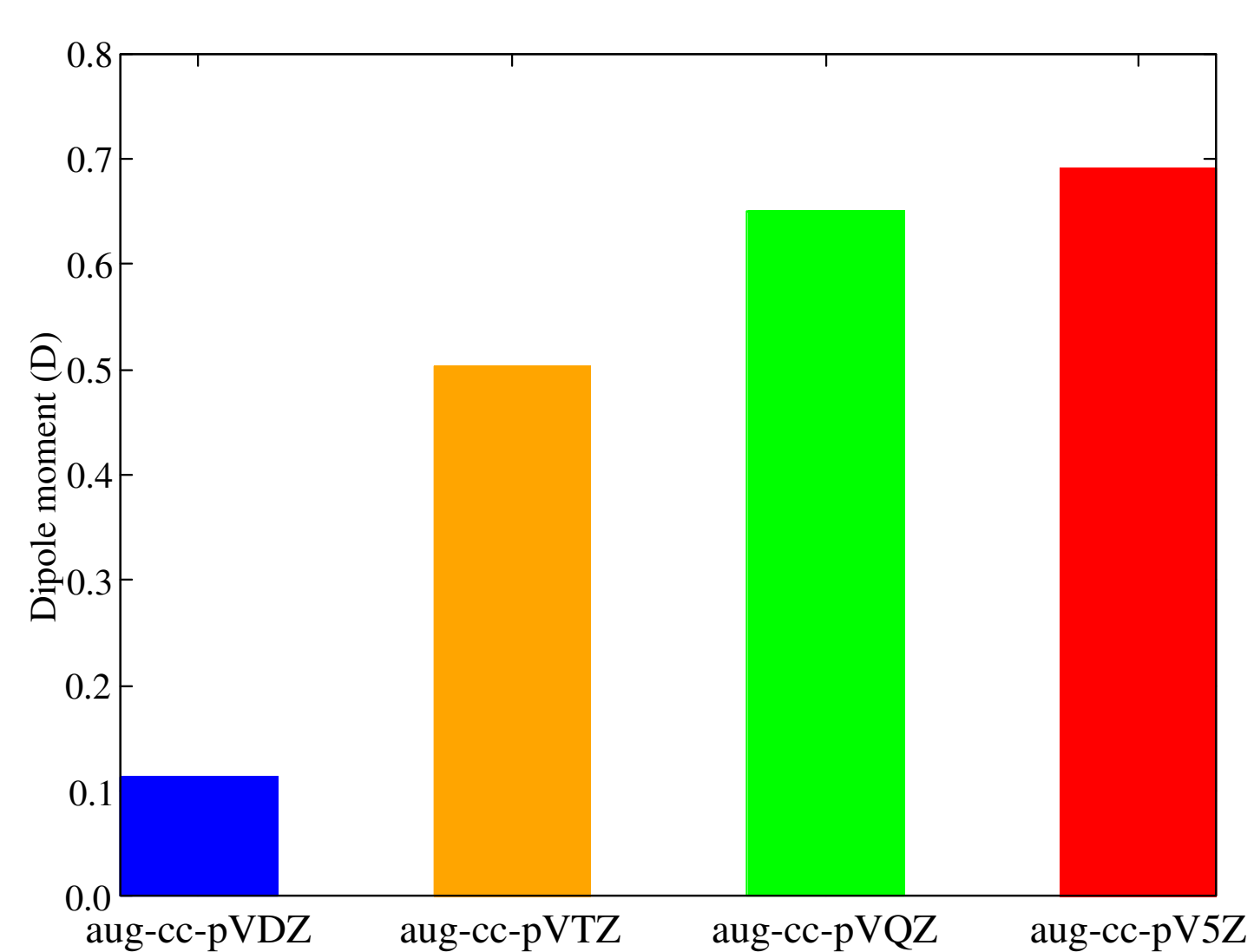


Figure 1. H<sub>2</sub>S, dipole moment of the first excited state in increasingly large basis sets with LR-CCSD [4].

As shown in Fig. 1, the dipole moments may be highly basis set dependent. Consequently, obtaining near complete basis set (CBS) limit values requires calculations with an increasingly larger number of one-electron basis functions.

## Formalism dependency

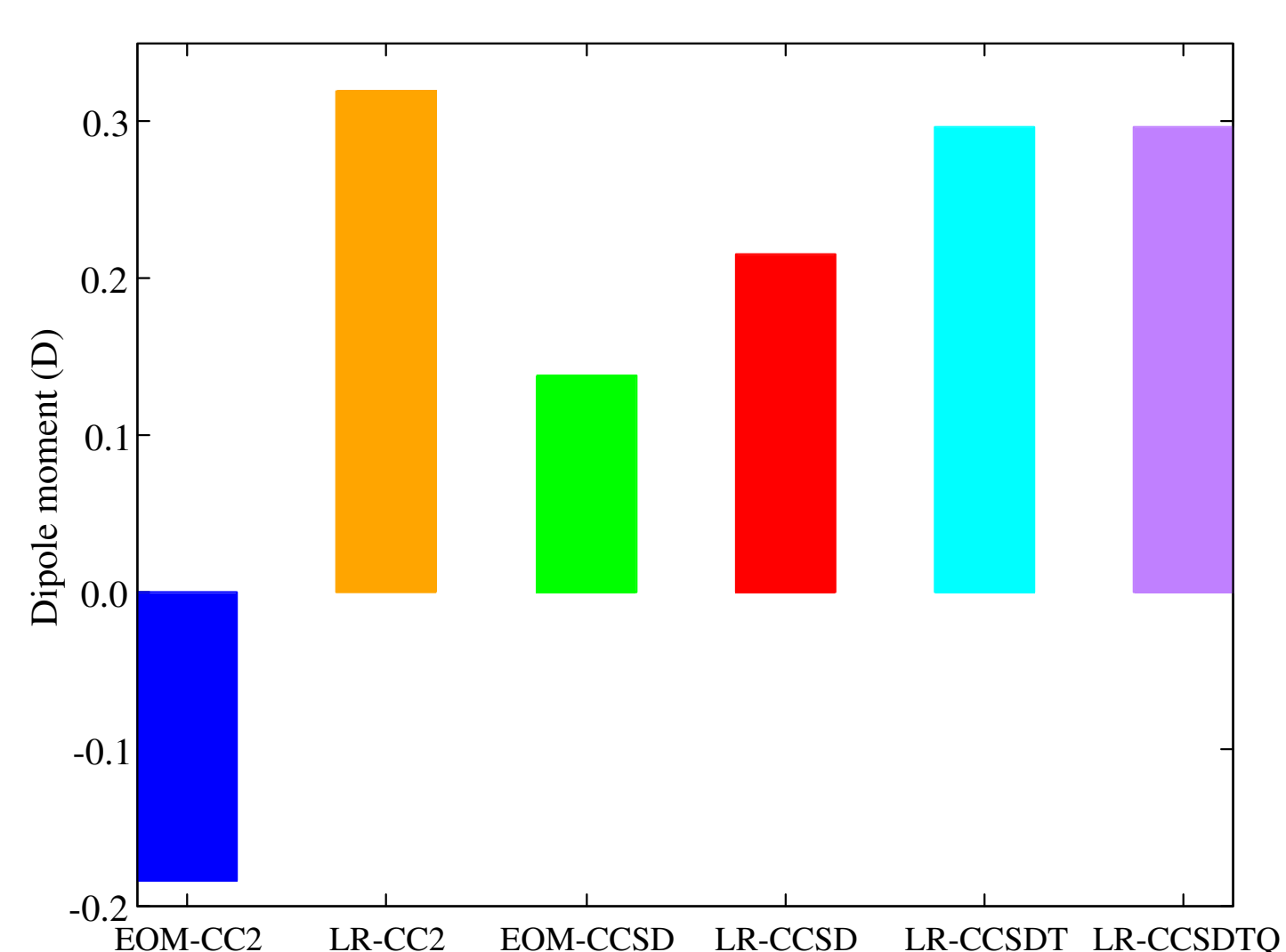


Figure 2. BF/aug-cc-pVTZ, dipole moment of the first excited state obtained with various formalisms [5].

In addition to the high basis set dependency, the quality of the dipole moments strongly depends on the formalism as shown in Fig. 2. Hence, to obtain near-FCI values, it is necessary to perform very accurate calculations, generally using high-order CC methods.

## CIPSI

CIPSI is a selected CI algorithm, which selects iteratively the most energetically-important determinants of the Hilbert space using a perturbative criterion [1, 2]. The process is illustrated in Fig. 3.

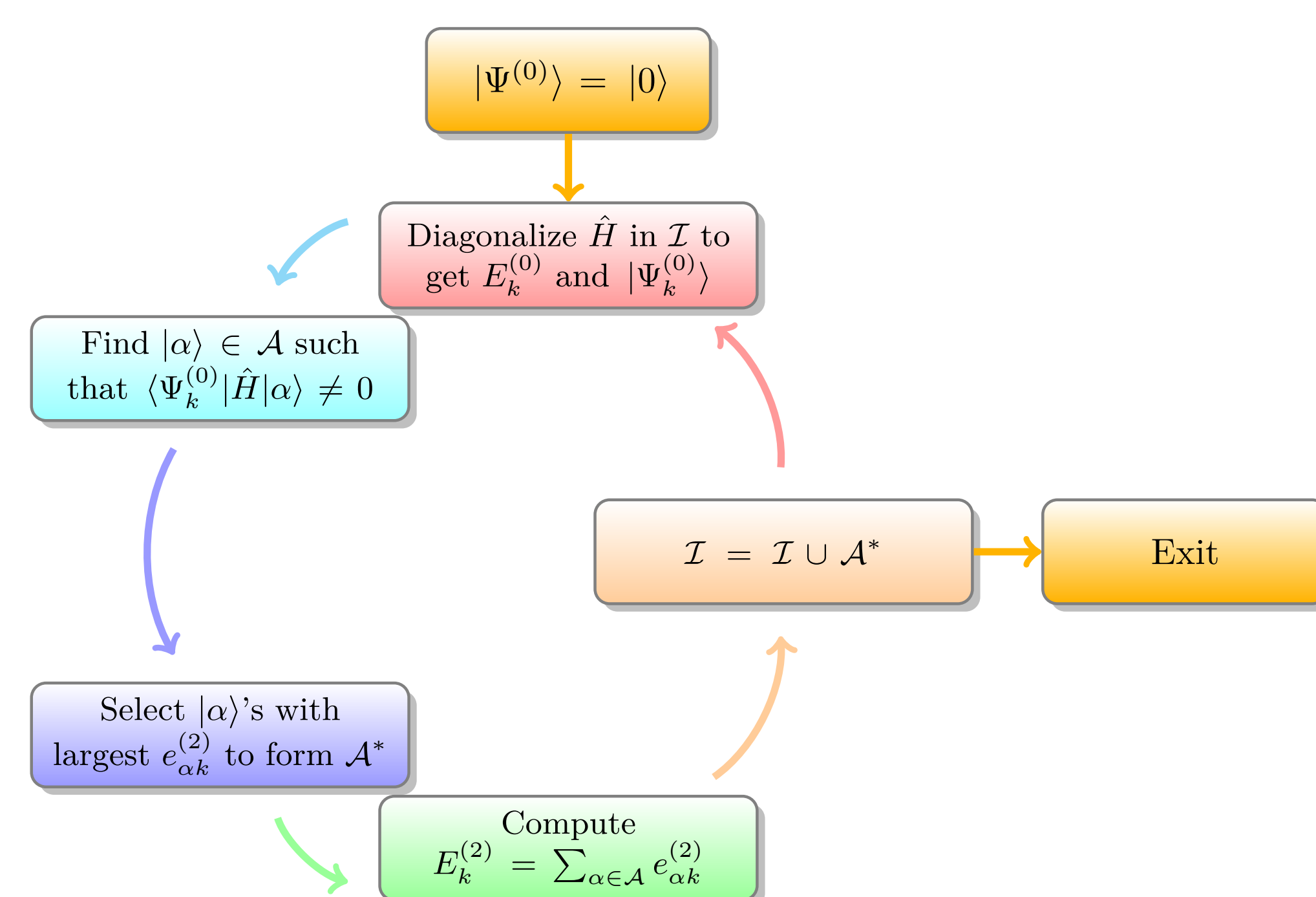


Figure 3. CIPSI algorithm.

## Extrapolation with CIPSI

The dipole moments and oscillator strengths are computed in CIPSI with the variational wave function  $\Psi_k^{(0)}$ . More accurate values can be obtained via extrapolation to the FCI limit, i.e.,  $E_k^{(2)} = \sum_{\alpha} e_{\alpha k}^{(2)} \rightarrow 0$ .

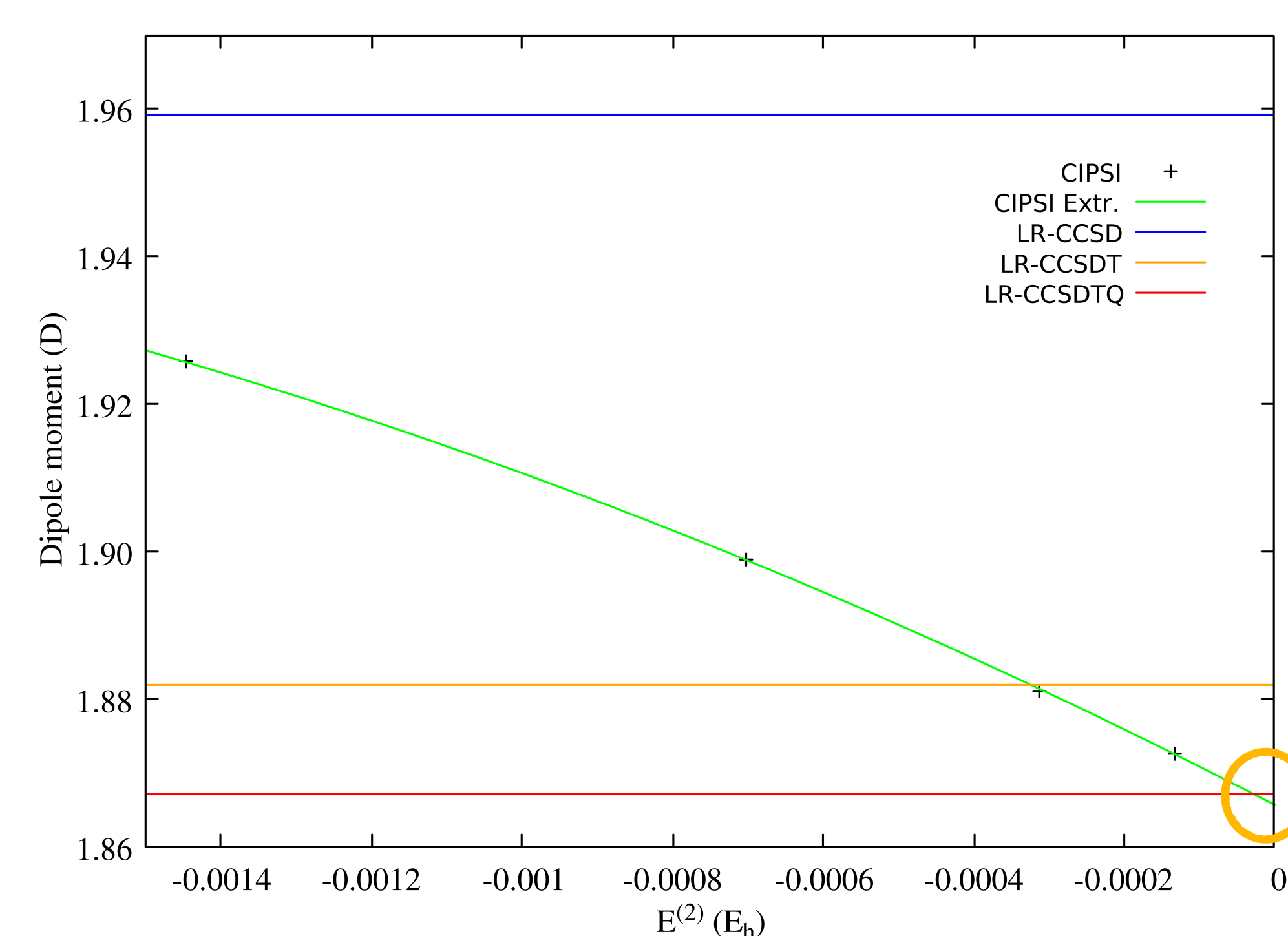


Figure 4. H<sub>2</sub>S/aug-cc-pVTZ, evolution of the dipole moment of the second excited state as a function of the second-order perturbative energy. The results are compared with the LR-CCSD, LR-CCSDT and LR-CCSDTQ values.

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## References

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