Problems in Linear Response and Equation of Motion formalisms

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Linear Response / Equation of Motion

In linear response (LR) and equation of motion (EOM) the following generalized eigenvalue problem is solved,

$$\left(\boldsymbol{E}^{[2]} - \omega \boldsymbol{S}^{[2]}\right)\boldsymbol{X} = \boldsymbol{0}\,, \tag{1}$$

where the Hessian and metric matrices are defined as

$$\boldsymbol{E}^{[2]} = \begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{pmatrix}, \quad \boldsymbol{S}^{[2]} = \begin{pmatrix} \boldsymbol{\Sigma} & \boldsymbol{0} \\ \boldsymbol{0} & -\boldsymbol{\Sigma}^* \end{pmatrix} \tag{2}$$

The submatrices are defined according to

$$A_{IJ} = \left\langle 0 \left| \left[\hat{R}_I^\dagger, \left[\hat{H}, \hat{R}_J\right]\right] \right| 0 \right\rangle \tag{3}$$

$$B_{IJ} = \left\langle 0 \left| \left[\hat{R}_I^\dagger, \left[\hat{H}, \hat{R}_J^\dagger\right]\right] \right| 0 \right\rangle \tag{4}$$

$$\Sigma_{IJ} = \left\langle 0 \left| \left[\hat{R}_I^\dagger, \hat{R}_J\right] \right| 0 \right\rangle \tag{5}$$

With four different LR/EOM parameterizations[1],

$$\hat{R}_I^{\text{naive}} = \hat{G}_I \tag{6}$$

$$\hat{R}_I^{\text{proj}} = \hat{G}_I \left|0\right\rangle \left\langle 0\right| - \left\langle 0 \left| \hat{G}_I \right| 0 \right\rangle \tag{7}$$

$$\hat{R}_I^{\text{sc}} = \boldsymbol{U}\hat{G}_I\boldsymbol{U}^\dagger \tag{8}$$

$$\hat{R}_I^{\text{st}} = \boldsymbol{U}\hat{G}_I \left|\text{HF}\right\rangle \left\langle 0\right| \tag{9}$$

All of the parameterizations are implemented in SlowQuant[2].

Wave function parameterization

The unitary coupled cluster wave function is parameterized as,

$$\left|\text{UCC}(\boldsymbol{\theta})\right\rangle = \exp\left(\sum_I \theta_I \left(\hat{T}_I - \hat{T}_I^\dagger\right)\right)\left|\text{HF}\right\rangle \tag{10}$$

Orbital rotations parameterization can be introduced as an integral transformation.The ground-state energy is found my performing a minimization over both types of parameters,

$$E_{\text{gs}} = \min_{\boldsymbol{\theta},\boldsymbol{\kappa}} \left\langle \text{UCC}(\boldsymbol{\theta}) \left| \hat{H}(\boldsymbol{\kappa}) \right| \text{UCC}(\boldsymbol{\theta}) \right\rangle \tag{11}$$

A parameter might be redundant,

$$E_{\text{gs}} = \min_{\{\boldsymbol{\theta},\boldsymbol{\kappa}\}\setminus P} \left\langle \text{UCC}(\boldsymbol{\theta}) \left| \hat{H}(\boldsymbol{\kappa}) \right| \text{UCC}(\boldsymbol{\theta}) \right\rangle \Bigg|_{P\in\mathbb{R}} \tag{12}$$

That is, a parameter is redundant if the ground-state energy can be recovered for any value of the parameter.

Helium atom

For the Helium atom in 6-31G the FCI expansion can be reached using UCCSD,

$$\left|\text{FCI}\right\rangle = \exp\left(\theta_1\left(\hat{T}_1 - \hat{T}_1^\dagger\right) + \theta_2\left(\hat{T}_2 - \hat{T}_2^\dagger\right)\right)\left|\text{HF}\right\rangle \tag{13}$$

$$= c_0\left|1100\right\rangle + \frac{c_1}{\sqrt{2}}\left(\left|1001\right\rangle - \left|0110\right\rangle\right) + c_2\left|0011\right\rangle \tag{14}$$

Changing the orbital rotation parameter does not change E_{gs},

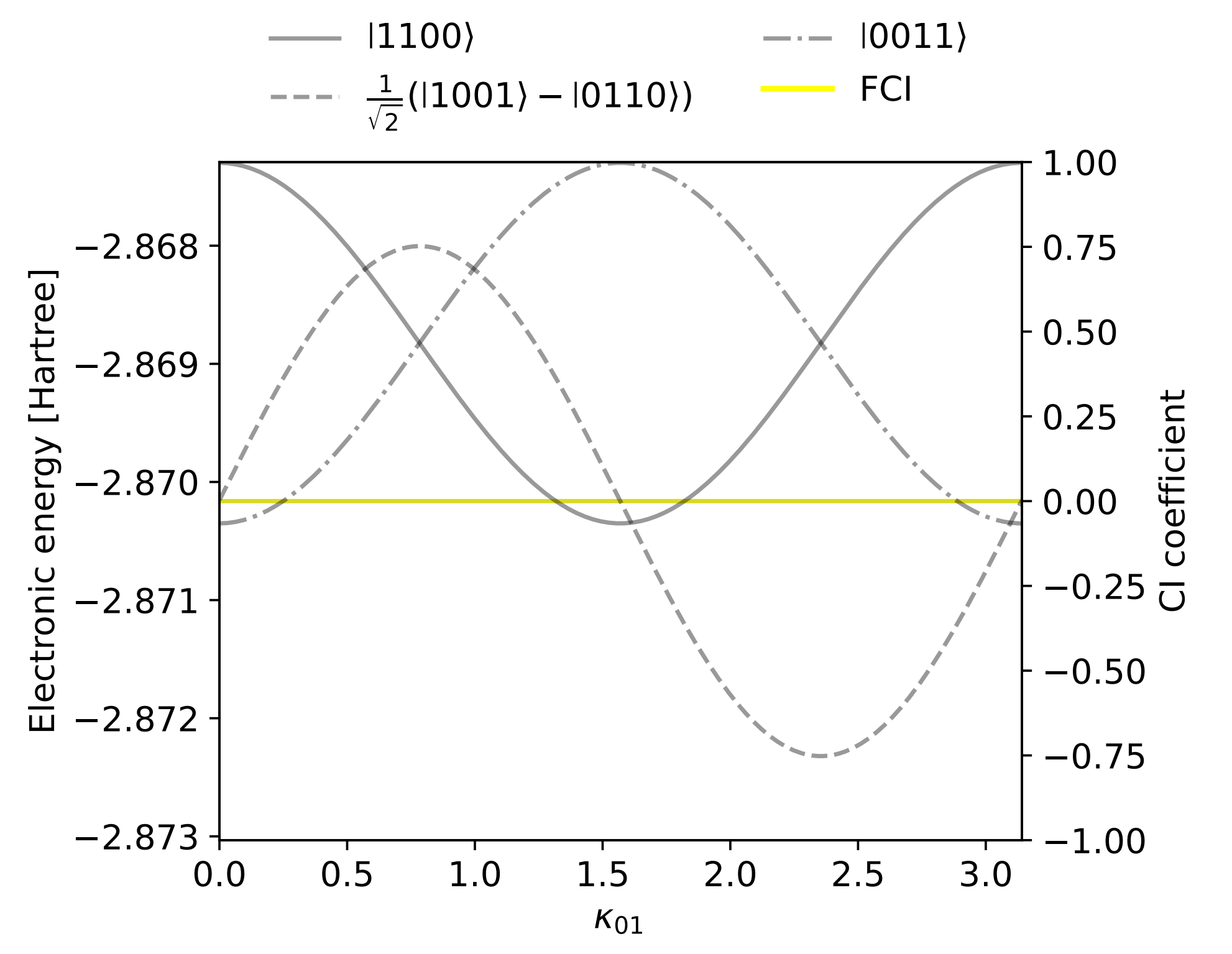

Figure 1: The CI coefficients from the FCI solution of the helium atom using the 6-31G basis set as a function of the redundant orbital rotation κ_{01}. The case of $\kappa_{01} = 0$ corresponds to Hartree-Fock orbitals. Note that the energy is shown to highlight that it can be held constant with respect to change in κ_{01}.[3]

The naive and projected parameterizations have a metric matrix, Eq. (2), that is different from identity.

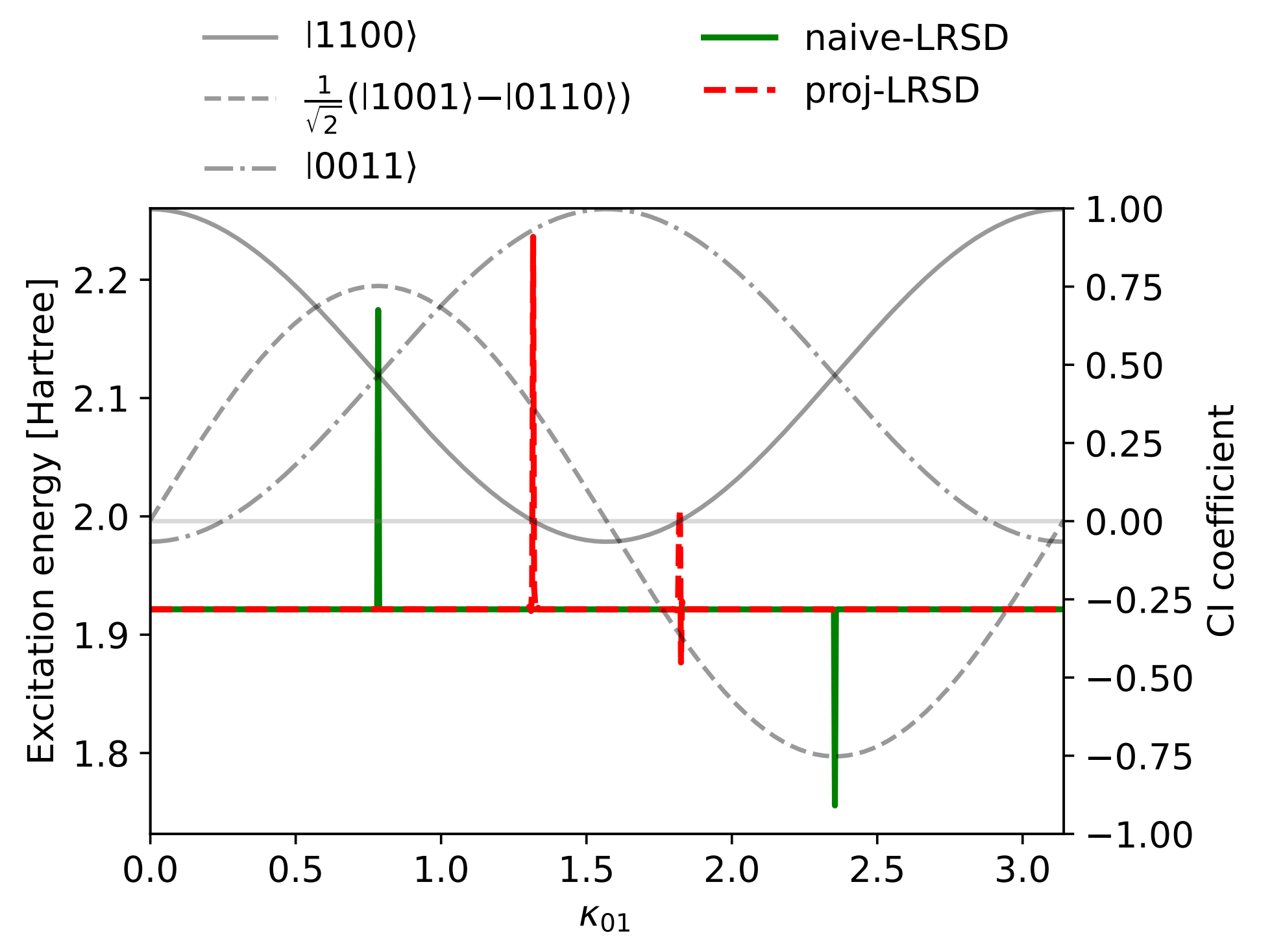

Figure 2: The lowest singlet excitation energy of the helium atom using the 6-31G basis set as a function of the redundant orbital rotation parameter κ_{01}. $\kappa_{01} = 0$ is the Hartree-Fock solution.[3]

The metric can become singular for naive-LR and proj-LR, resulting in wrong excitation energies.

The effect of the redundant orbital rotation on calculated excitation energies becomes more pronounced when considering a truncated LR expansion.

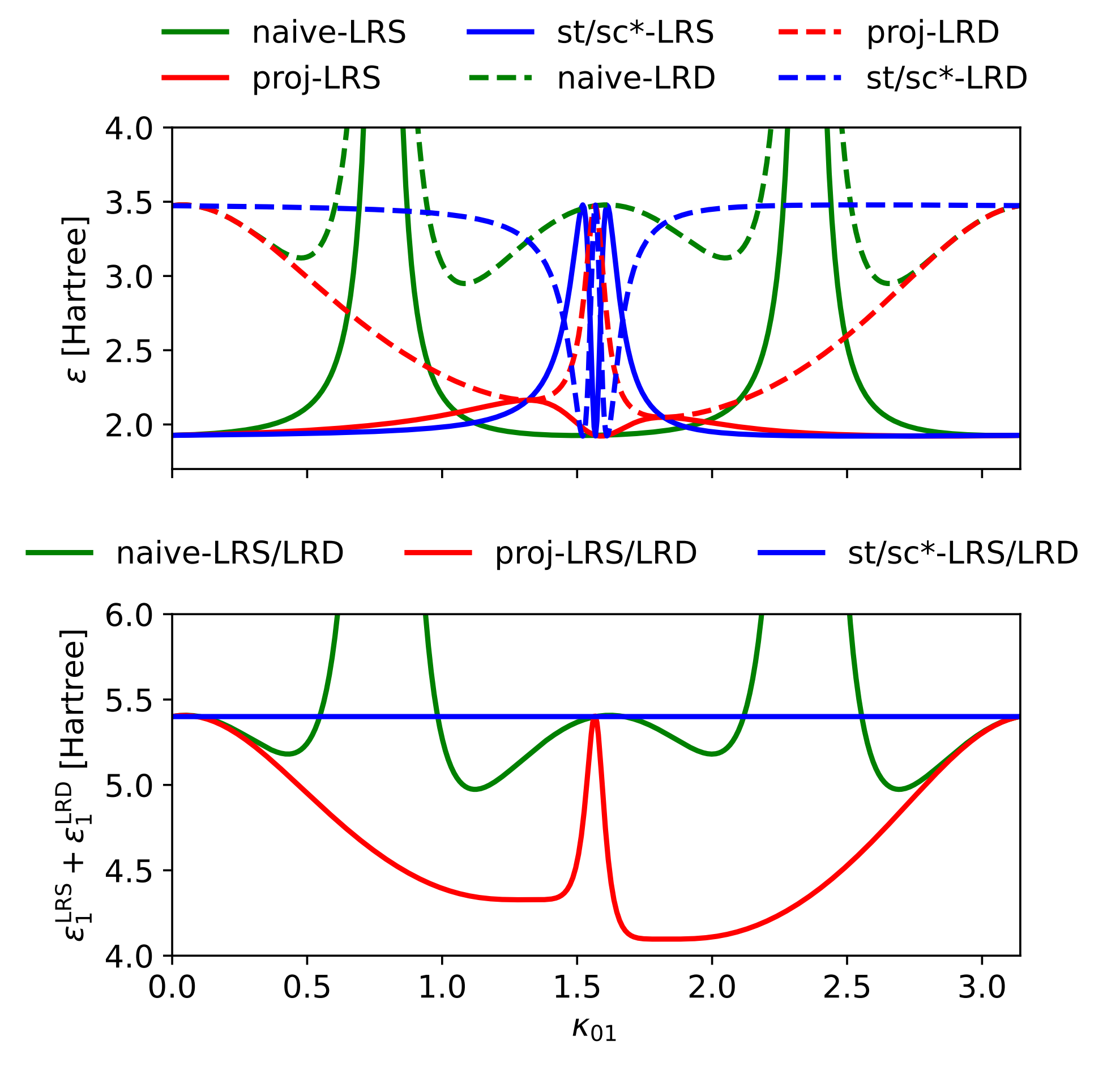

Figure 3: The singlet single excitation energy and singlet double excitation energy of the He atom calculated in the 6-31G basis set with LR singlet singles and LR singlet doubles, respectively, as a function of the redundant orbital rotation parameter κ_{01}.[4]

For st-LR the sum of excitation energies is conserved.

For the other parameterizations, the sum of excitation energies is not conserved.

Shot noise impact

In the context of quantum computing, calculating the matrix elements in the LR equations will have an associated shot-noise.

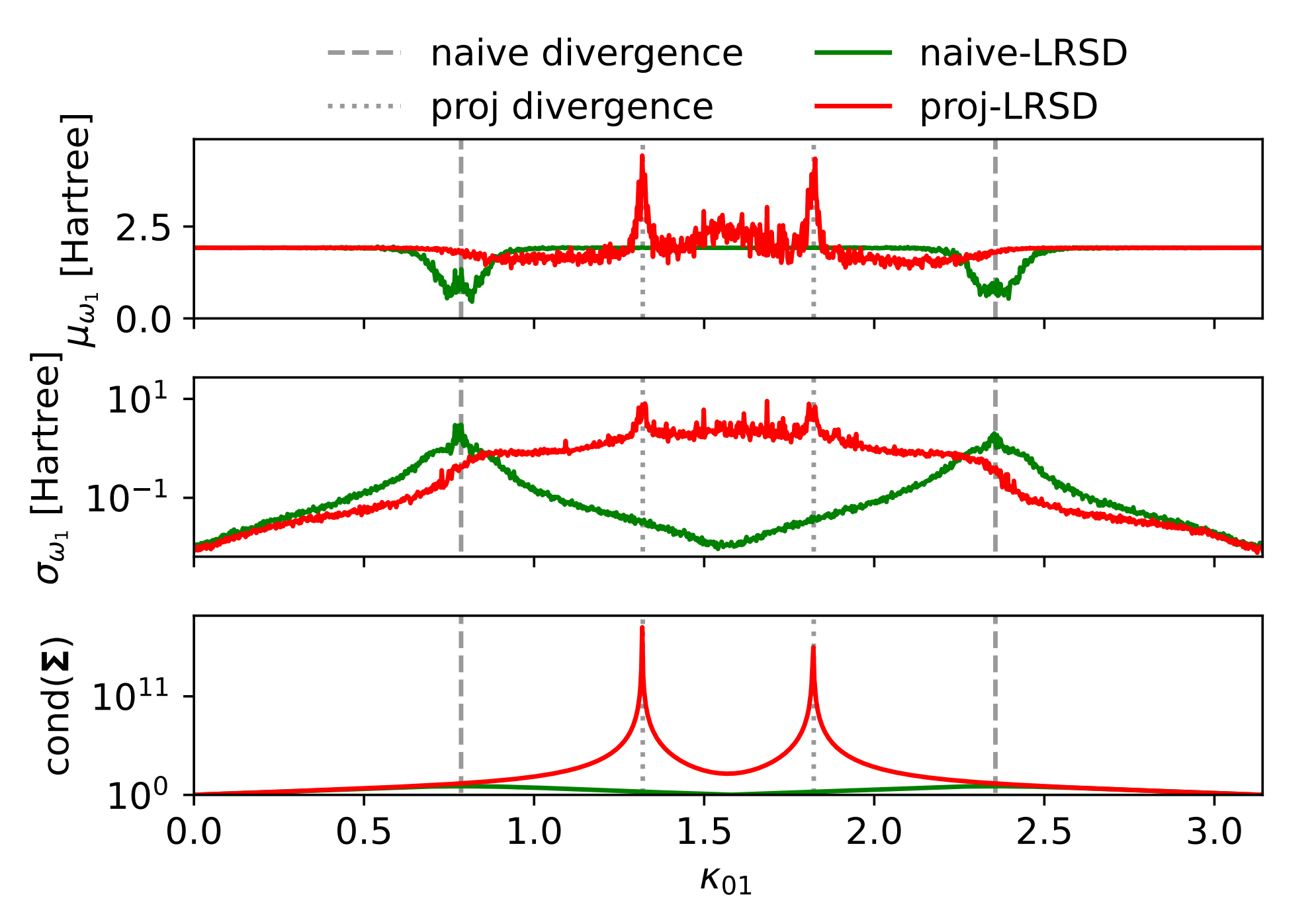

Figure 4: The mean value, μ_{ω_1}, and standard deviation, σ_{ω_1}, of the first excitation energy for the helium atom using the 6-31G basis set. The mean value and standard deviation are obtained on the basis of 100 calculations, each using 1000 shots. $\text{cond}\left(\boldsymbol{\Sigma}\right)$ is the condition number of $\boldsymbol{\Sigma}$ for the noiseless matrix, calculated using the L^2 norm. All quantities are reported as a function of the redundant orbital rotation κ_{01}.[3]

For systems with more than one orbital rotation parameter, the problem can be induced by maximizing the condition number of the metric,

$$\boldsymbol{\kappa}^{\text{div}} = \underset{\boldsymbol{\kappa}^{\text{red}}}{\arg\max}\left\{\text{cond}\left(\boldsymbol{\Sigma}\left(\boldsymbol{\kappa}^{\text{red}}\right)\right)\right\} \tag{15}$$

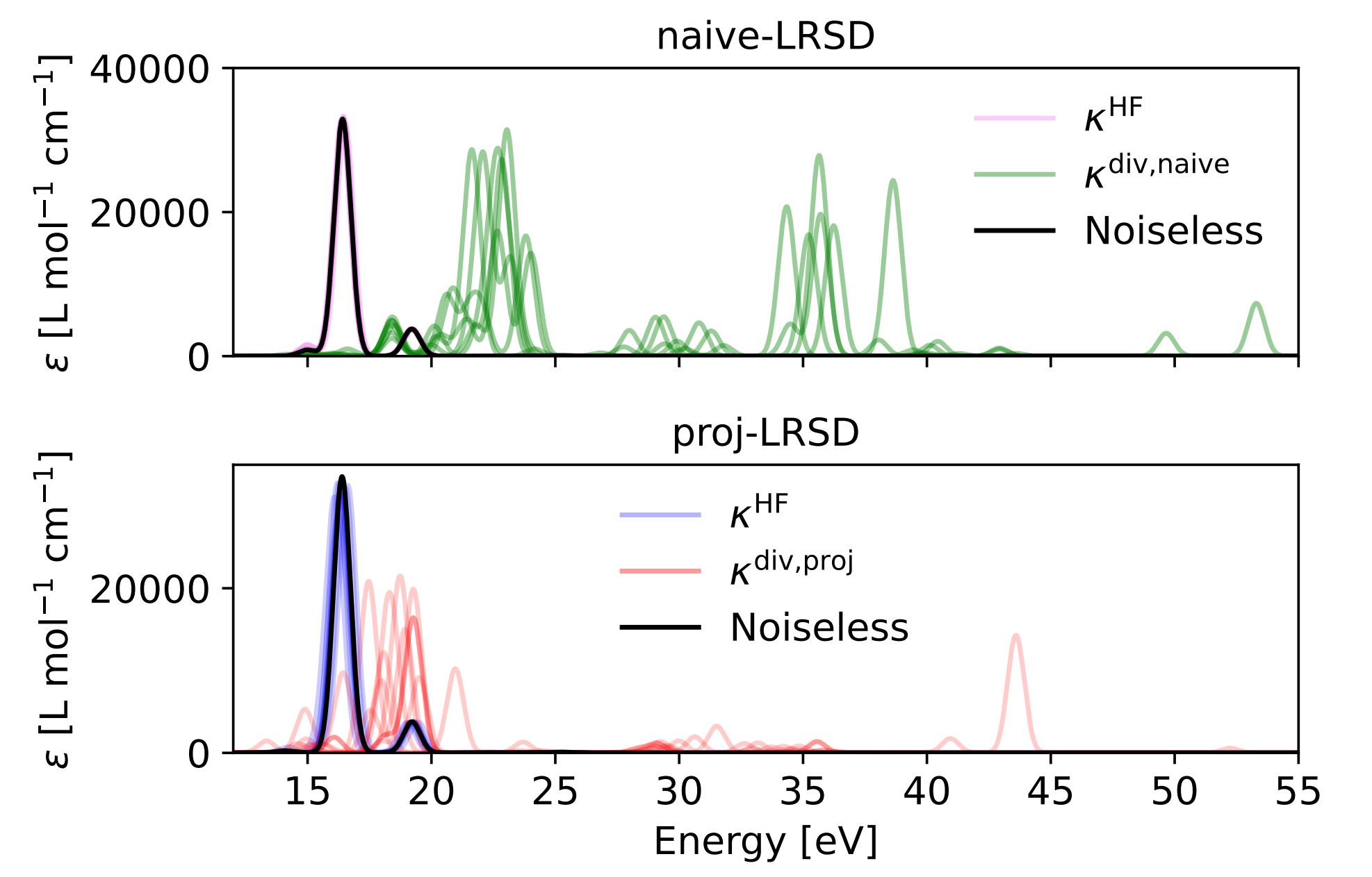

Figure 5: Calculated absorption spectra of H_4 using 100k shots on shot noise simulator. Each spectrum was calculated 10 times. The H_4 molecule is rectangular with the sides being 1.5 Å and 1.8 Å.[3]

The noise sensitivity of naive-LR and proj-LR depends significantly on the orbitals.

State-transfer LR

The st-LR takes the form of a unitary transformed Hamiltonian. The effect of redundant parameters on the excitation energies can thus be investigated by maximizing the trace of the LR equations.

$$\left\{\boldsymbol{\theta}^{\text{bad}}, \boldsymbol{\kappa}^{\text{bad}}\right\} = \underset{\boldsymbol{\theta},\boldsymbol{\kappa}}{\text{argmax}} \sum_{|I\rangle\in|\text{SS}\rangle} \left\langle I \left| \boldsymbol{U}_\theta^\dagger \boldsymbol{U}_\kappa^\dagger \hat{H} \boldsymbol{U}_\kappa \boldsymbol{U}_\theta \right| I \right\rangle \tag{16}$$

$$\text{subject to} \quad E_0 = \left\langle \text{HF} \left| \boldsymbol{U}_\theta^\dagger \boldsymbol{U}_\kappa^\dagger \hat{H} \boldsymbol{U}_\kappa \boldsymbol{U}_\theta \right| \text{HF} \right\rangle$$

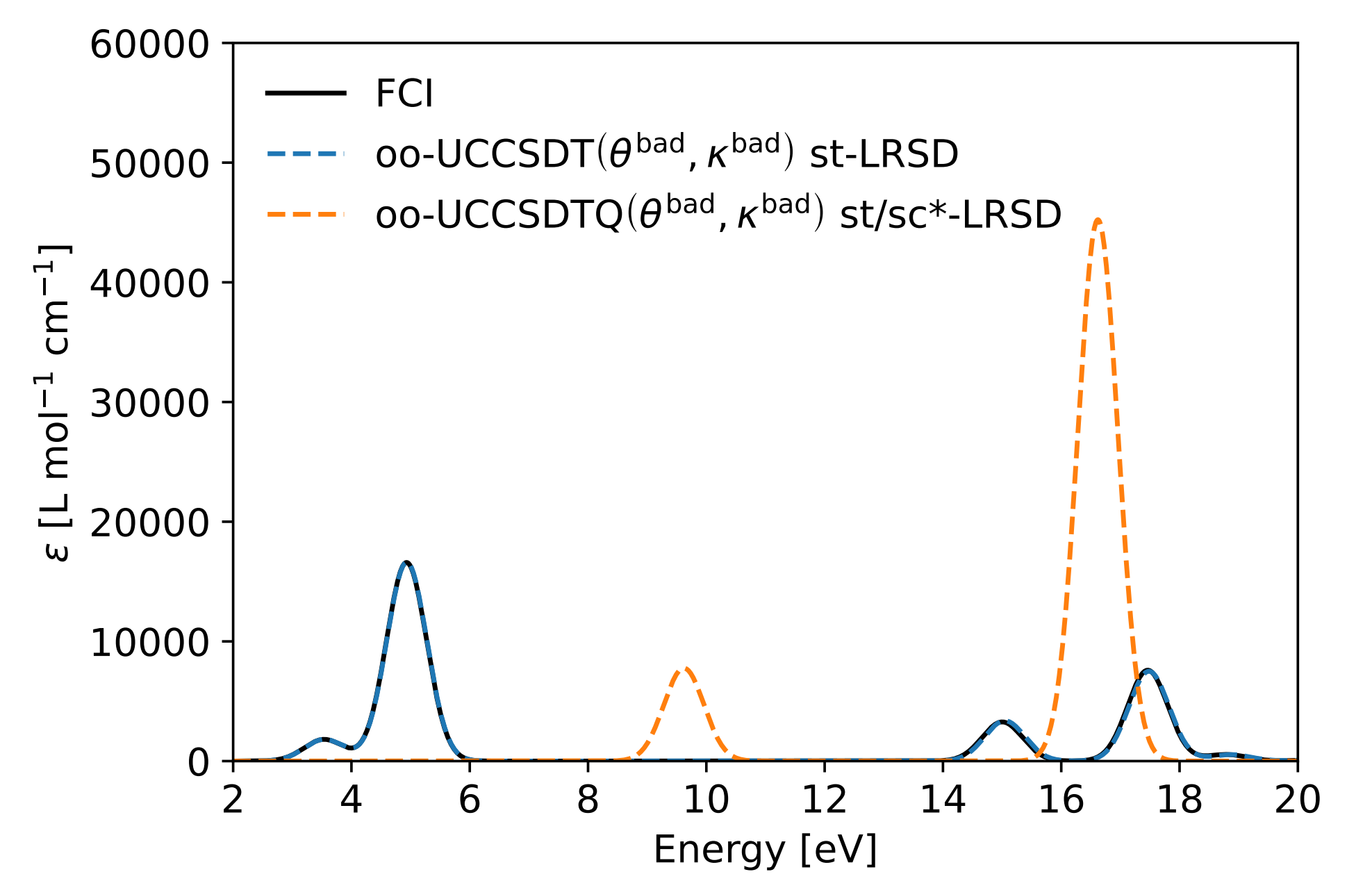

Figure 6: Calculated electronic spectra of LiH in the STO-3G basis using different levels of theory. The oo-UCCSD($\boldsymbol{\theta}^{\text{bad}}, \boldsymbol{\kappa}^{\text{bad}}$) spectrum is omitted from the figure as it is visually on top of the oo-UCCSDT($\boldsymbol{\theta}^{\text{bad}}, \boldsymbol{\kappa}^{\text{bad}}$) spectrum.[4]

By minimization instead of maximization in Eq. (16), this procedure can be used to improve the performance of small st-LR expansions.

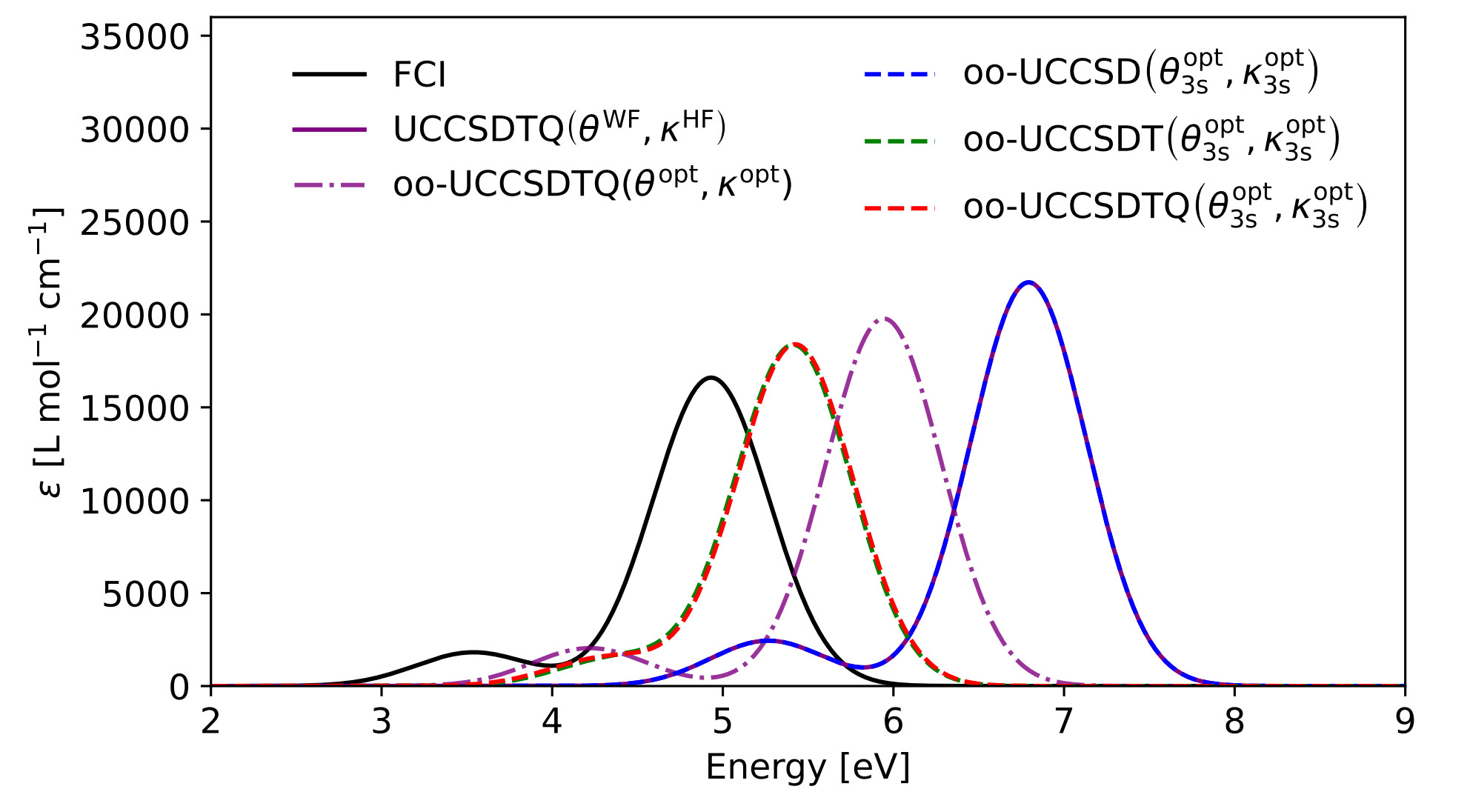

Figure 7: LiH/STO-3G. Spectra calculated with state-transfer LR singles (st-LRS) using various UCC wave functions, where the wave function parameters are constrained optimized for the first three excited states denoted with $(\boldsymbol{\theta}_{3s}^{\text{opt}}, \boldsymbol{\kappa}_{3s}^{\text{opt}})$. $\boldsymbol{\theta}^{\text{WF}}$ refers to the θ-values found by only optimizing for the ground-state. $\boldsymbol{\theta}^{\text{opt}}$ and $\boldsymbol{\kappa}^{\text{opt}}$ are parameters optimized for all 8 excitations in st-LRS.[4]

Constrained multi-state wave function optimization can be used to improve small LR expansions.

References

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[2] E Kjellgren and KM Ziems. SlowQuant, 2024.

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