Supplementary Information: Improving the efficiency of G_0W_0 calculations with approximate spectral decompositions of dielectric matrices: Supplementary information

Han Yang,[1,2] Marco Govoni,[2,3] and Giulia Galli[1,2,3,a)]

[1)] *Department of Chemistry, University of Chicago, Chicago, Illinois 60637, United States*

[2)] *Pritzker School of Molecular Engineering, University of Chicago, Chicago, Illinois 60637, United States*

[3)] *Materials Science Division and Center for Molecular Engineering, Argonne National Laboratory, Lemont, Illinois 60439, United States*

(Dated: 21 January 2022)

[a)] gagalli@uchicago.edu

This Supplementary Information reports convergence studies of the G_0W_0 calculations of the vertical ionization potential of the CH_4 molecule, whcih is taken as a representative example of the molecular systems studied in the main text.

G_0W_0 CALCULATIONS OF THE VERTICAL IONIZATION POTENTIAL OF THE METHANE MOLECULE

A. Eigenvalues of the symmetrized *irreducible* density-density response function

In Fig. 1, we compare eigenvalues for the symmetrized irreducible density-density response function of the methane molecule: 500 stdPDEPs and 100 stdPDEPs + 400 kinPDEPs. On the scale of the figure the results are indistinguishable.

B. Calculations of the vertical ionization potential

We present, in Fig. 2, the results for the vertical ionization potential of the CH_4 molecule computed with 5, 10, 20 standard PDEPs (N_{stdPDEP}), and the remaining 100, 200, 300 and 400 PDEPs treated as kinetic PDEPs. When setting $N_{\mathrm{stdPDEP}} = 10$ or 20 we obtain results accurate within 0.02 eV, as compared to the ones obtained using only standard PDEP. When using 5 stdPDEPs we obtain instead an error more than 10 times larger (0.25 eV).

C. Interpolation of results

In this work, the computed energy levels were interpolated with respect to the total number of PDEPs,

$$E = a + \frac{b}{N_{\mathrm{stdPDEP}} + N_{\mathrm{kinPDEP}}}, \tag{1}$$

where a is the converged energy level and b is an arbitrary number depending on the system.

In Fig. 3, we show results for the vertical ionization potential of the methane molecule with respect to the total number of PDEPs included in the calculation: 20 stdPDEPs were used followed by 0, 100, 200, 300, 400 kinPDEPs. We note that as the number of kinPDEPs increases, one obtains energies similar to those computed with stdPDEPs; in addition the

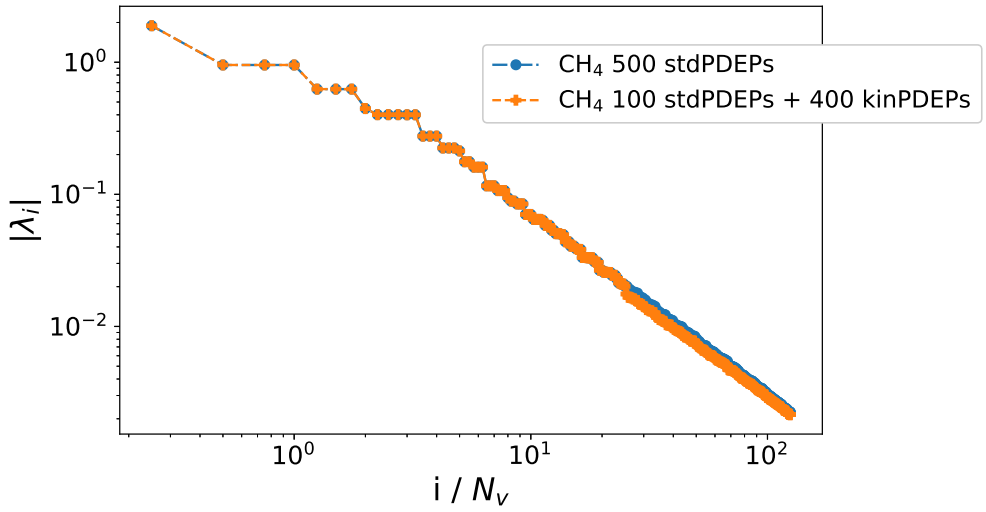

FIG. 1. Comparison between the eigenvalues (λ_i) of the leading 500 stdPDEPs and the eigenvalues of the 100 leading stdPDEPs followed by 400 kinPDEPs of the CH4 molecule. N_v is the number of occupied states and stdPDEPs and kinPDEPs are eigenvectors of the symmetrized irreducible density-density response function($\tilde{\chi}_0$) solved using Kohn-Sham Hamiltonian and kinetic operator.

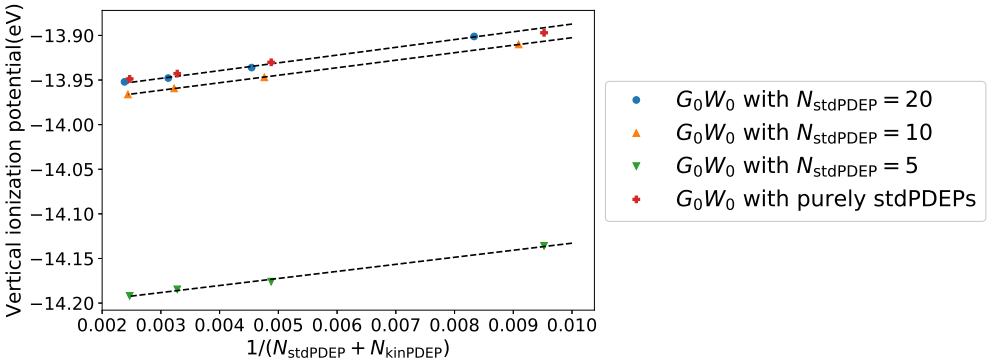

FIG. 2. Calculations of the vertical ionization potential of the methane molecule with 20, 10, 5 standard eigenpotentials (stdPDEP) and up to 400 kinetic eigenpotentials (kinPDEP) compared to calculations (red symbols) performed with purely stdPDEPs.

proportionality between energies and the inverse of the total number of PDEPs holds even when the total number of PDEPs in small.

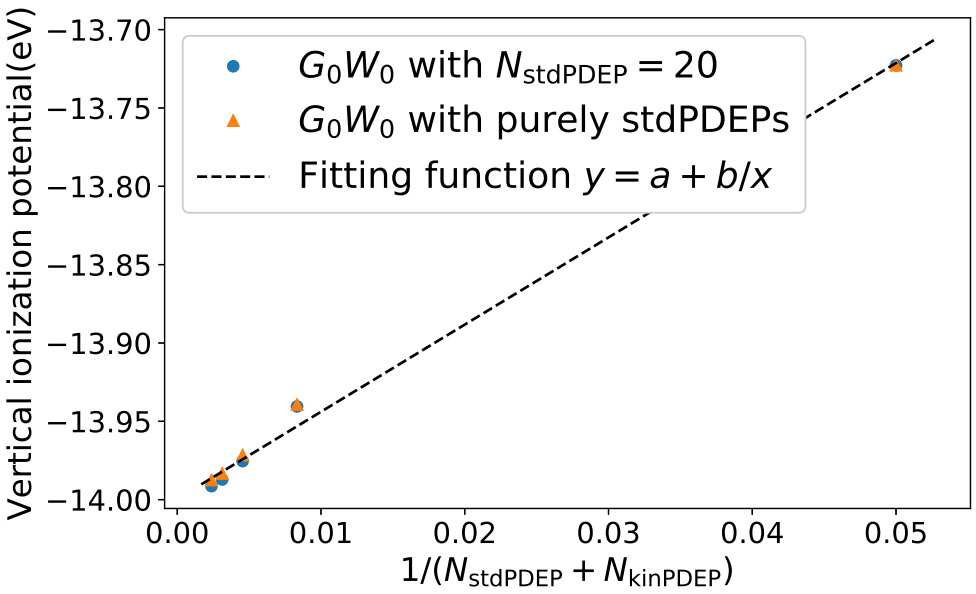

FIG. 3. Interpolation of the computed vertical ionization potential of the methane molecule with respect to the total number of PDEPs, where PDEPs are eigenvectors of the symmetrized irreducible density-density response function ($\tilde{\chi}_0$).