Reference energies for valence ionizations and satellite transitions

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Laboratoire de Chimie et Physique Quantiques, Toulouse

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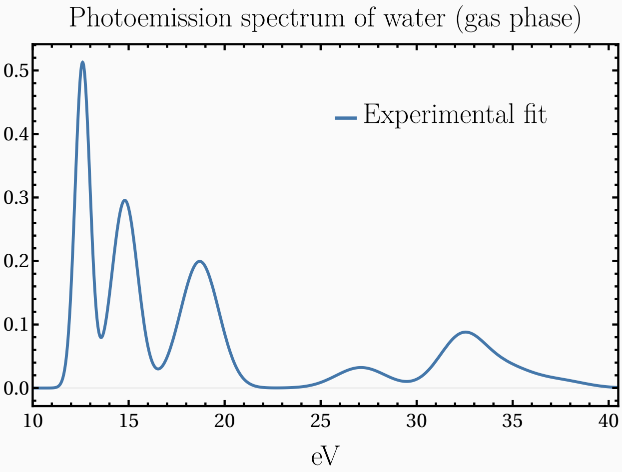
Experimental spectrum of water



Ning *et al.*, Chem. Phys. 343 (2008) 19-30

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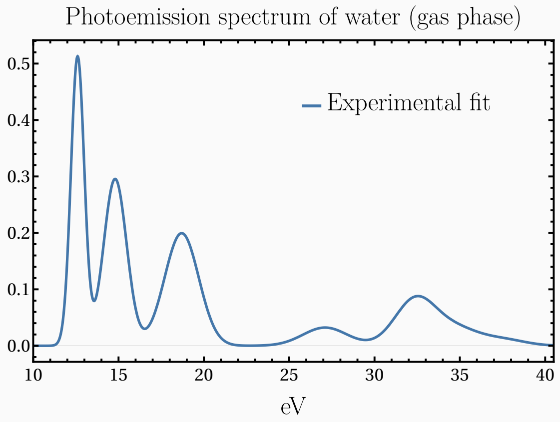
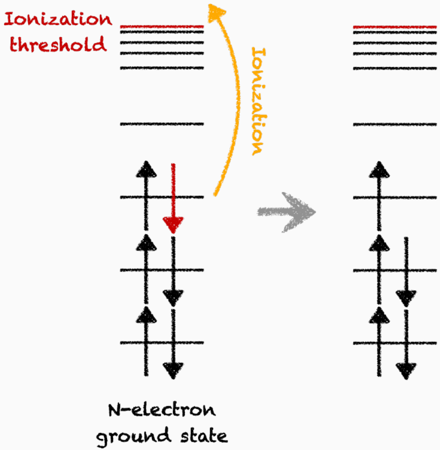
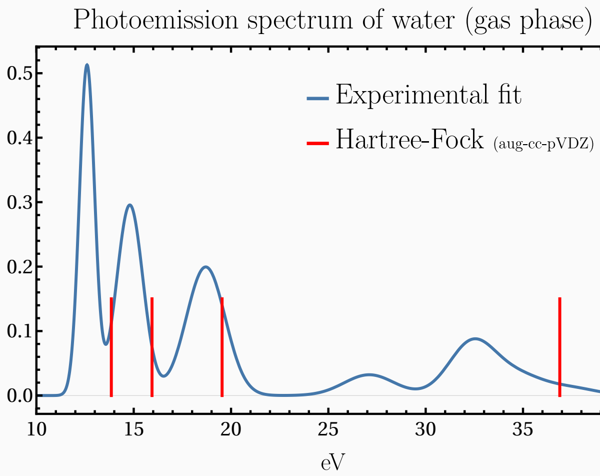




Hartree-Fock spectrum



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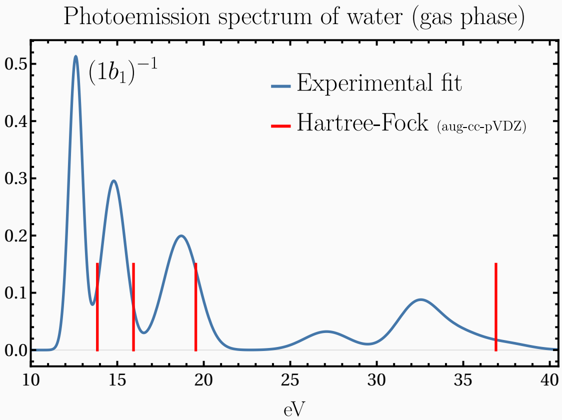

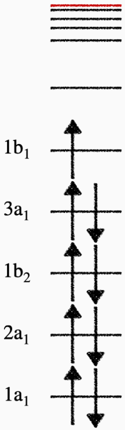

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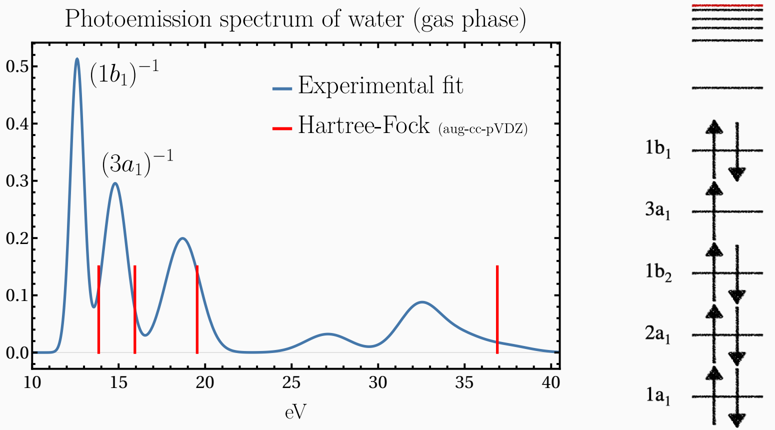

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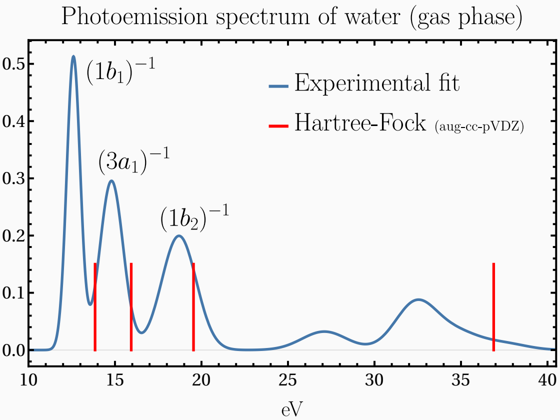

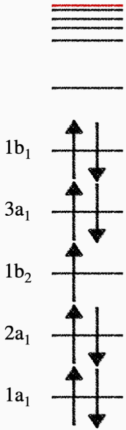

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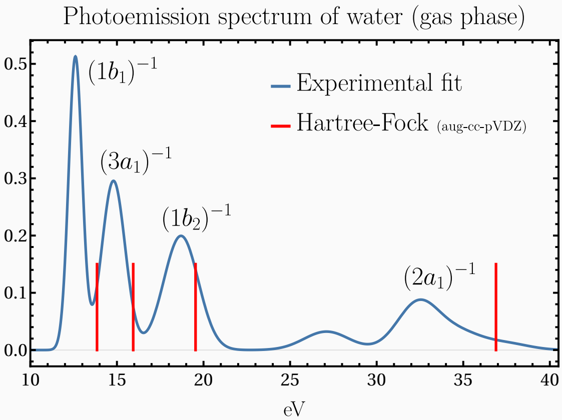

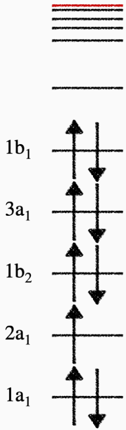

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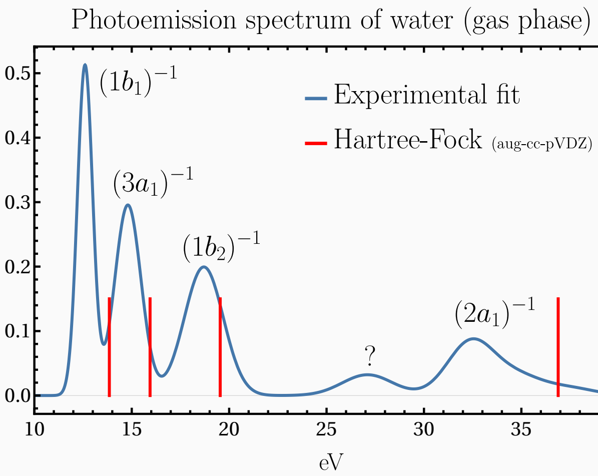
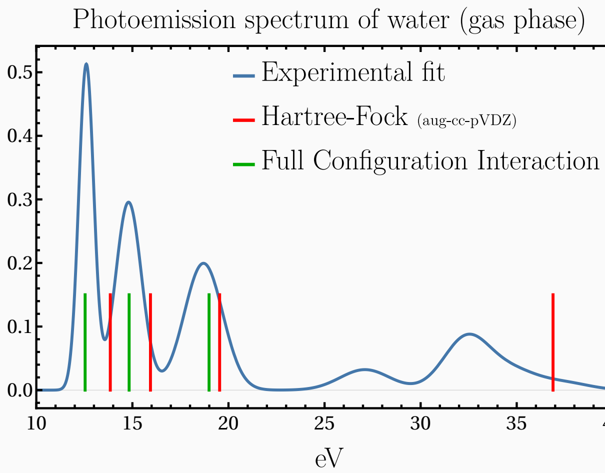


Full Configuration Interaction spectrum



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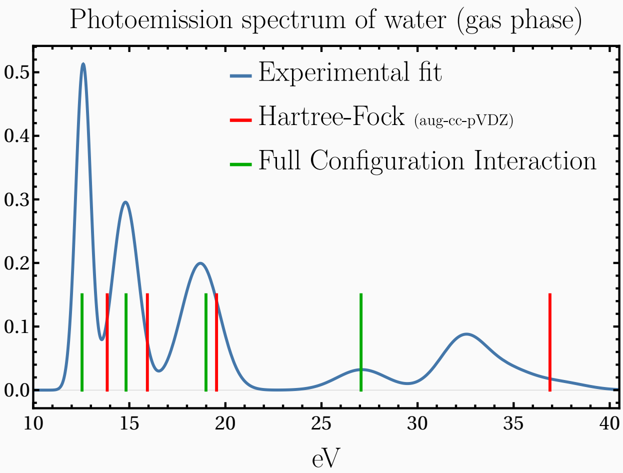

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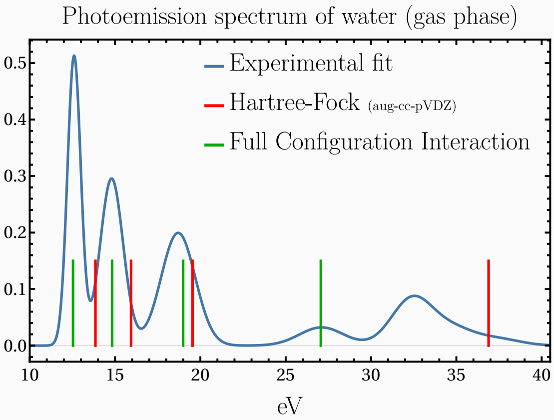

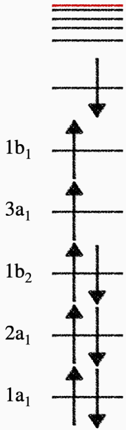

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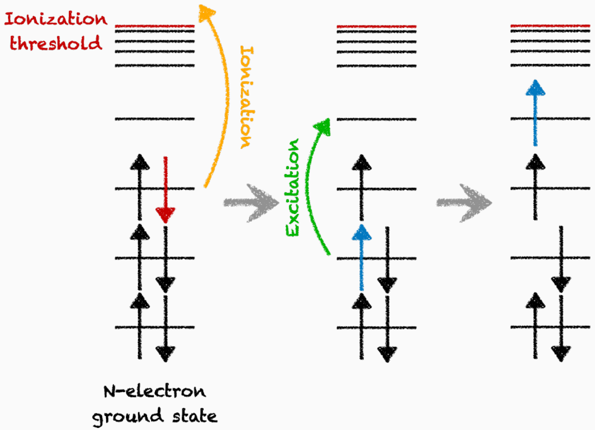
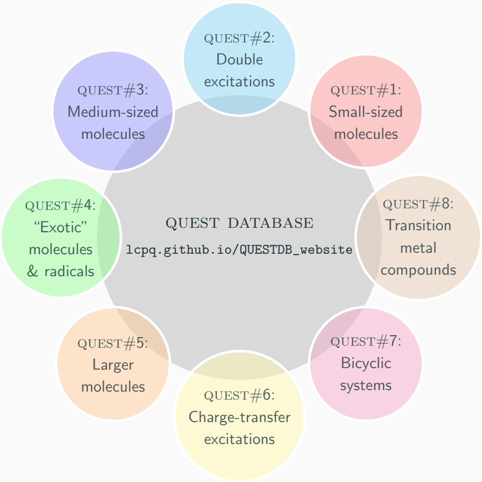


The Quest Project



Veril *et al.*, WIREs Comput. Mol. Sci., 11 (2021) e1517

Selected CI

The Configuration Interaction Wavefunction

$$\left|\Psi_0^{\text{CI}}\right\rangle = \left|\Phi_0\right\rangle + \sum_{ia} c_i^a \left|\Phi_i^a\right\rangle + \sum_{ijab} c_{ij}^{ab} \left|\Phi_{ij}^{ab}\right\rangle + \sum_{ijkabc} c_{ijk}^{abc} \left|\Phi_{ijk}^{abc}\right\rangle + \ldots \quad (1)$$

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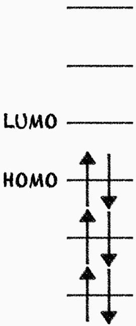

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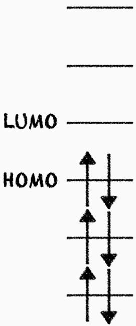

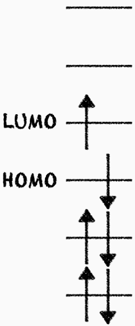

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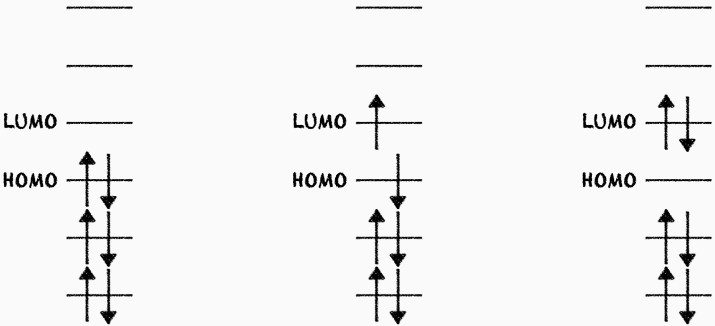

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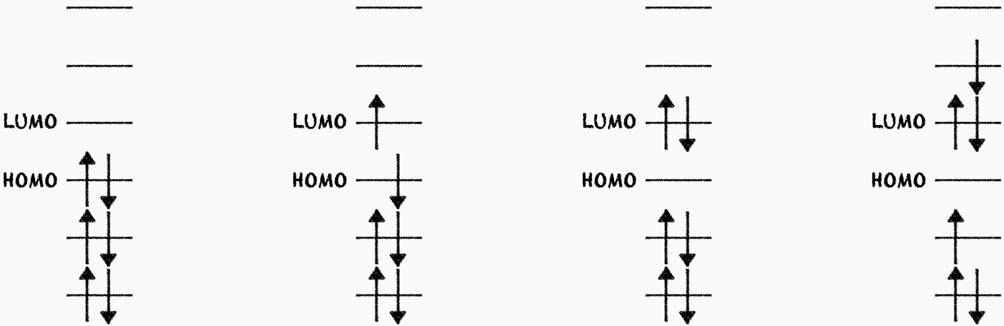

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$$\left|\Psi_0^{\text{CI}}\right\rangle = \underbrace{\left|\Phi_0\right\rangle + \sum_{ia} c_i^a \left|\Phi_i^a\right\rangle}_{\text{CIS}} + \sum_{ijab} c_{ij}^{ab} \left|\Phi_{ij}^{ab}\right\rangle + \sum_{ijkabc} c_{ijk}^{abc} \left|\Phi_{ijk}^{abc}\right\rangle + \ldots \tag{1}$$

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The selected CI wavefunction

Idea: Select only the most important determinant in each excitation class!

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Many flavours: CIPSI, shCI, asCI, FCIQMC, ...

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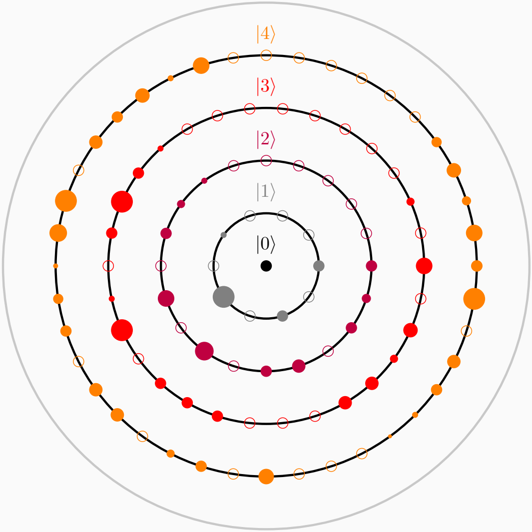
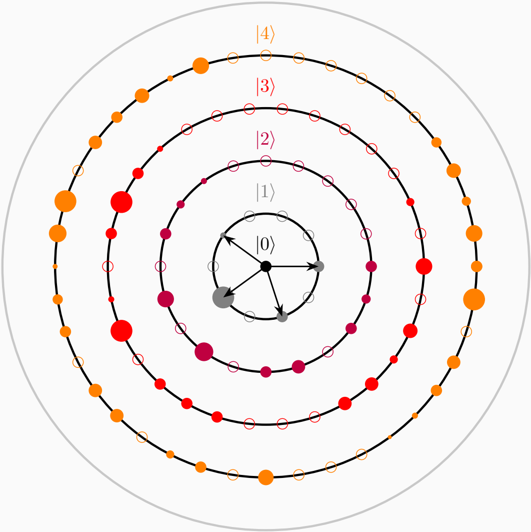
Garniron *et al.*, J. Chem. Theory Comput. 15 (2019) 3591

Hilbert space exploration



Hilbert space exploration



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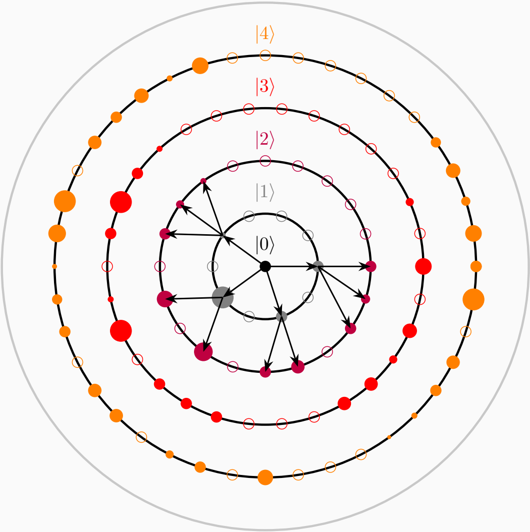

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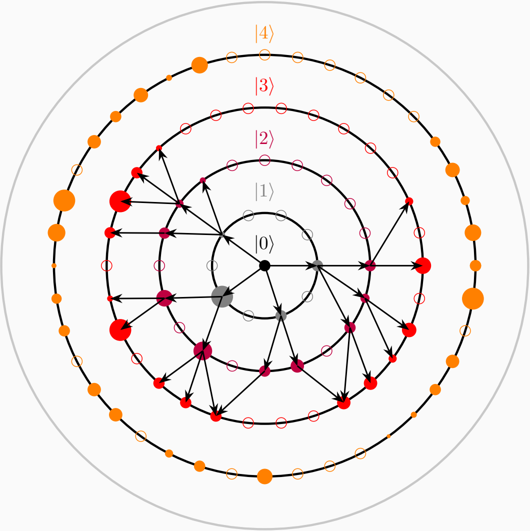

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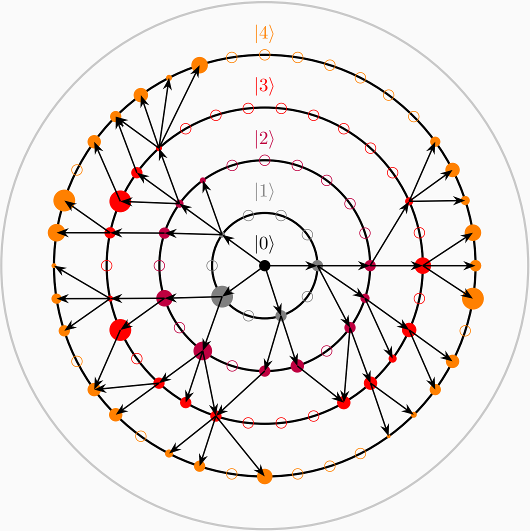
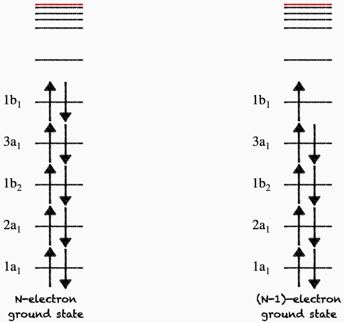


Charged excitation energies with selected CI

First ionization potential

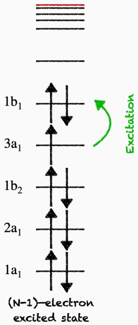
$$E_{\text{1st IP}} = \left(E_0^N - E_0^{N-1}\right) \quad (2)$$



Charged excitation energies with selected CI

Valence ionization and satellites

$$E_{\text{IP/Sat}} = E_{\text{1st IP}} + E_i^{N-1} \quad (2)$$



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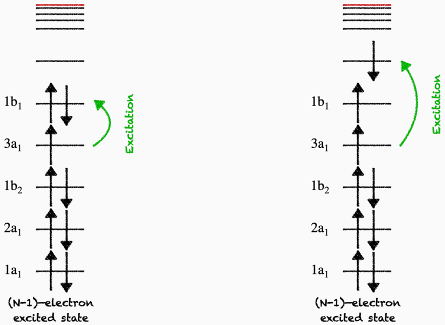

Coupled-cluster hierarchy

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Scaling of the coupled-cluster hierarchy

Methods	CCSD	CCSDT	CCSDTQ
Scaling	N^6	N^8	N^{10}

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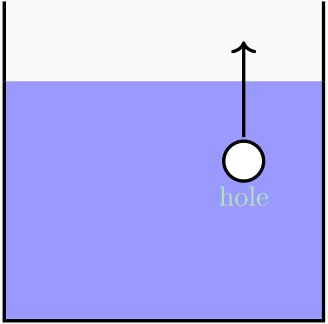
Approximate coupled-cluster hierarchy

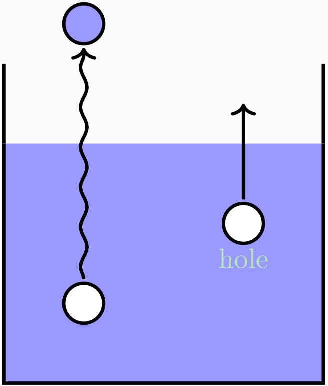
Methods	CC2	CC3	CC4
Scaling	N^5	N^7	N^9

The GW approximation (Hedin, Phys. Rev. 139 (1965) A796)



electron removal

The *GW* approximation (Hedin, Phys. Rev. 139 (1965) A796)



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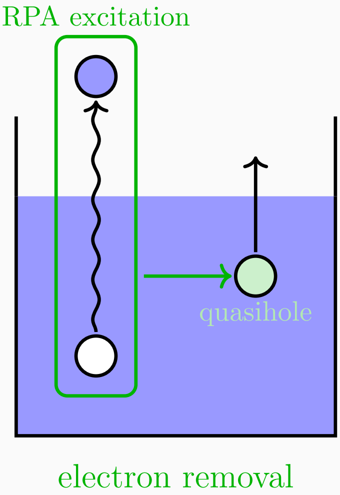


Our set of molecules

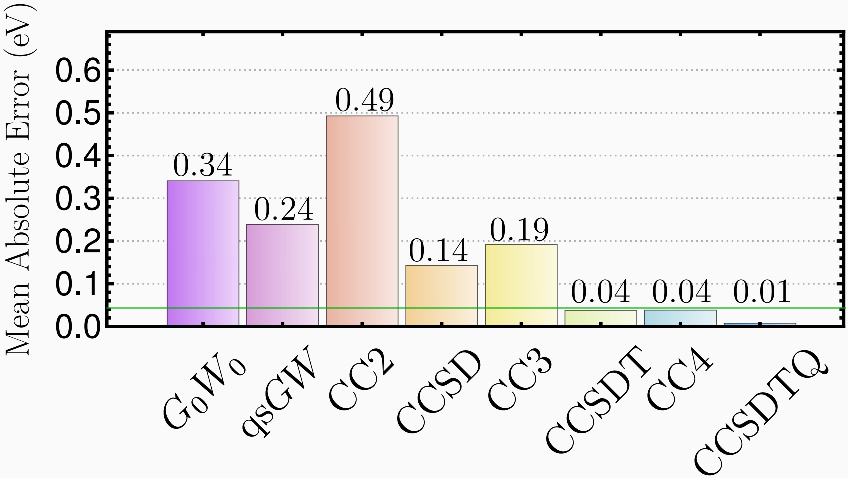
8 electrons	10 electrons
BH_3	Ne, HF, H_2O, NH_3, CH_4

12 electrons	14 electrons	16 electrons
LiF, BeO, C_2	BF, CO, N_2	CH_2O

18 electrons	20 electrons	22 electrons
Ar, HCl, H_2S, F_2	LiCl	CO_2, CS

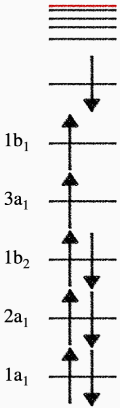
20 molecules, 49 IPs, 35 Satellites

Statistics for IP



The first satellite of water

Methods	*GW*	CC3	CCSDT	CC4	CCSDTQ	Exact
Satellite (eV)	30.85	34.72	27.48	27.49	27.10	27.06



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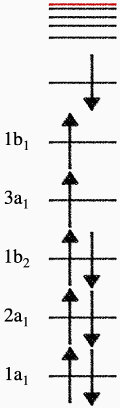
Post-*GW* self-energies?

- Able to describe satellites
- Do no deteriorate results for IPs!



Questions?

Static Version of *GW*

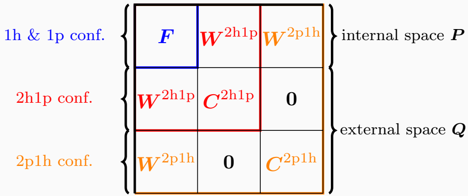
$$\left[\mathbf{F} + \boldsymbol{\Sigma}^{GW}\left(\omega = \epsilon_p^{GW}\right)\right]\varphi_p^{GW} = \epsilon_p^{GW}\varphi_p^{GW}$$

$$\boldsymbol{\Sigma}^{GW}(\omega) = \mathbf{W}^{\text{2h1p}}\left(\omega\mathbf{1} - \mathbf{C}^{\text{2h1p}}\right)^{-1}\left(\mathbf{W}^{\text{2h1p}}\right)^{\dagger} + \mathbf{W}^{\text{2p1h}}\left(\omega\mathbf{1} - \mathbf{C}^{\text{2p1h}}\right)^{-1}\left(\mathbf{W}^{\text{2p1h}}\right)^{\dagger}$$

downfolding ⇄ upfolding

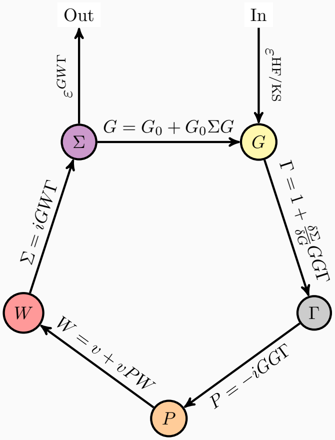
$$\mathbf{H}\Psi_p^{GW} = \epsilon_p^{GW}\Psi_p^{GW}$$

$$\mathbf{H} = \begin{pmatrix} \mathbf{F} & \mathbf{W}^{\text{2h1p}} & \mathbf{W}^{\text{2p1h}} \\ (\mathbf{W}^{\text{2h1p}})^{\dagger} & \mathbf{C}^{\text{2h1p}} & \mathbf{0} \\ (\mathbf{W}^{\text{2p1h}})^{\dagger} & \mathbf{0} & \mathbf{C}^{\text{2p1h}} \end{pmatrix}$$



Bintrim & Berkelbach, JCP 154 (2021) 041101; Monino & Loos JCP 156 (2022) 231101; Tolle & Chan, JCP 158 (2023) 124123

Hedin's Pentagon



Hedin, Phys Rev 139 (1965) A796

The wonderful equations of Hedin

$$\underbrace{G(12)}_{\text{Green's function}} = G_0(12) + \int G_0(13)\Sigma(34)G(42)d(34)$$

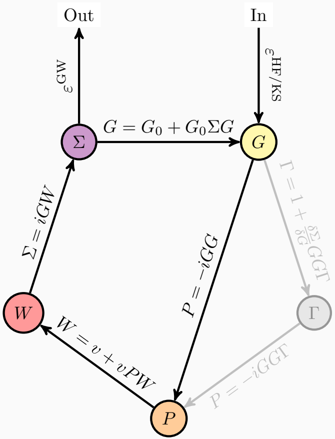
$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i \int G(13)\Gamma(342)G(41)d(34)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

$$\underbrace{\Sigma(12)}_{\text{self-energy}} = i \int G(14)W(13)\Gamma(423)d(34)$$

Hedin's Square



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The *GW* approximation

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$$\underbrace{\Gamma(123)}_{\text{vertex}} = \delta(12)\delta(13) + \cancel{\int \frac{\delta\Sigma(12)}{\delta G(45)} G(46)G(75)\Gamma(673)d(4567)}$$

$$\underbrace{P(12)}_{\text{polarizability}} = -i\cancel{\int} G(12)\cancel{\Gamma(342)}G(21)\cancel{d(34)} = -iG(12)G(21)$$

$$\underbrace{W(12)}_{\text{screening}} = v(12) + \int v(13)P(34)W(42)d(34)$$

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