GW, BSE, eDFT, RPA, and piña colada

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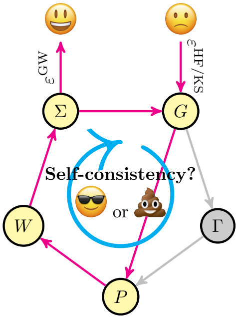
Gori-Giorgi Symposium

Section 1

Many-body perturbation theory



arXiv:2002.04514 [physics.chem-ph]

Pros and Cons of the Bethe-Salpeter Formalism for Ground-State Energies

Pierre-François Loos,[1,*] Anthony Scemama,[1,†] Ivan Duchemin,[2,‡] Denis Jacquemin,[3,§] and Xavier Blase[4,¶]

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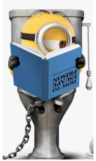
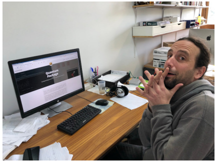
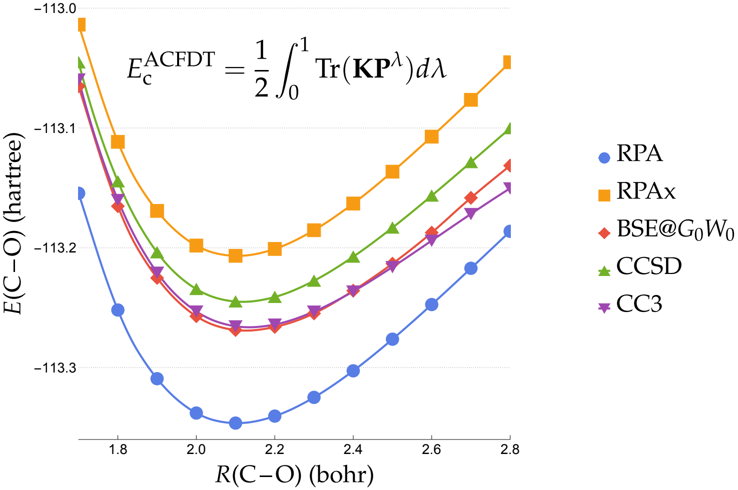



Ground-state potential energy surface of CO/cc-pVQZ



BSE correlation energy via ACFDT:

$$\boxed{E_c^{\text{BSE}} = \frac{1}{2} \int_0^1 \text{Tr}\left(\mathbf{K}\mathbf{P}^{\lambda}\right) d\lambda}$$

Correlation part of the two-electron density matrix:

$$\mathbf{P}^{\lambda} = \begin{pmatrix} \mathbf{Y}^{\lambda}(\mathbf{Y}^{\lambda})^{\mathsf{T}} & \mathbf{Y}^{\lambda}(\mathbf{X}^{\lambda})^{\mathsf{T}} \\ \mathbf{X}^{\lambda}(\mathbf{Y}^{\lambda})^{\mathsf{T}} & \mathbf{X}^{\lambda}(\mathbf{X}^{\lambda})^{\mathsf{T}} \end{pmatrix} - \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}$$

"Casida"-like equations:

$$\begin{pmatrix} \mathbf{A}^{\lambda} & \mathbf{B}^{\lambda} \\ -\mathbf{B}^{\lambda} & -\mathbf{A}^{\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{X}_m^{\lambda} \\ \mathbf{Y}_m^{\lambda} \end{pmatrix} = \Omega_m^{\lambda} \begin{pmatrix} \mathbf{X}_m^{\lambda} \\ \mathbf{Y}_m^{\lambda} \end{pmatrix}$$

with

$$A_{ia,jb}^{\lambda,\text{BSE}} = \delta_{ij}\delta_{ab}(\epsilon_a^{GW} - \epsilon_i^{GW}) + \lambda\left[2(ia|jb) - W_{ij,ab}^{\lambda}\right]$$

$$B_{ia,jb}^{\lambda,\text{BSE}} = \lambda\left[2(ia|bj) - W_{ib,aj}^{\lambda}\right]$$

Screened Coulomb operator:

$$W^{\lambda}_{ij,ab}(\omega) = (ij|ab) + 2\sum_{m}^{OV} [ij|m]^{\lambda} [ab|m]^{\lambda} \left(\frac{1}{\omega - \Omega_m^{\lambda,\text{RPA}} + i\eta} - \frac{1}{\omega + \Omega_m^{\lambda,\text{RPA}} - i\eta} \right)$$

Screened two-electron integrals:

$$[pq|m]^{\lambda} = \sum_{i}^{O} \sum_{a}^{V} (pq|ia) (\mathbf{X}_m^{\lambda} + \mathbf{Y}_m^{\lambda})_{ia}$$

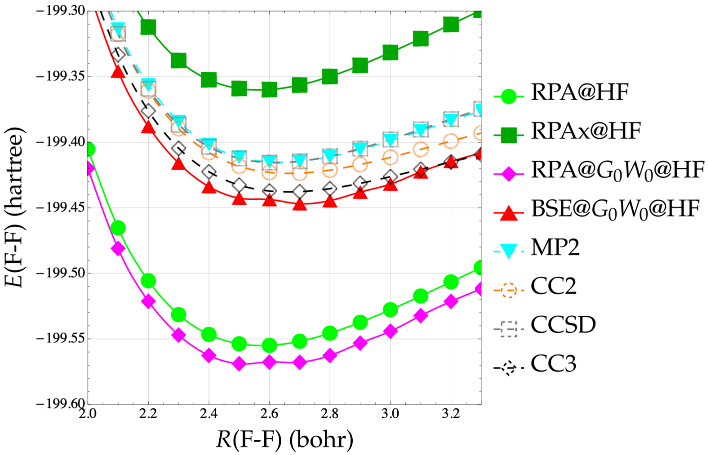


FIG. 4. Ground-state PES of F_2 around its equilibrium geometry obtained at various levels of theory with the cc-pVQZ basis set.

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Article

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Green Functions and Self-Consistency: Insights From the Spherium Model

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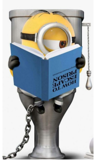

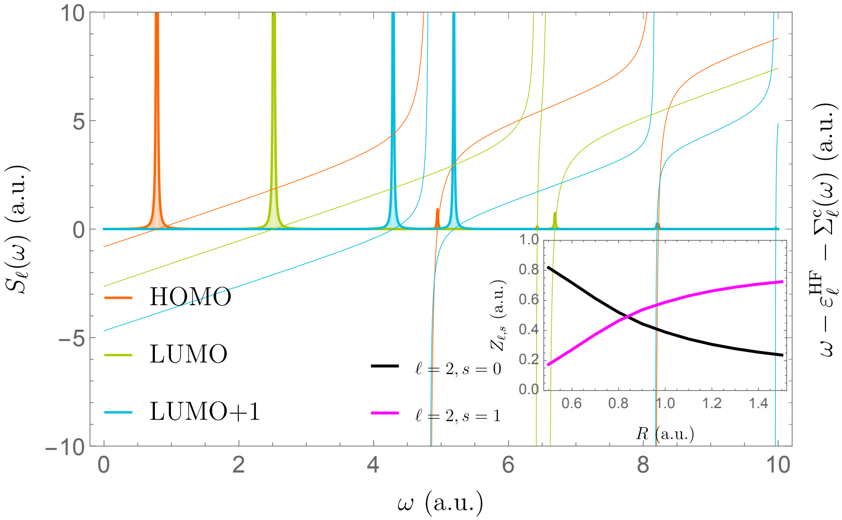

$S_\ell(\omega)$ (a.u.)
$\omega - \varepsilon_\ell^{\mathrm{HF}} - \Sigma_\ell^{\mathrm{c}}(\omega)$ (a.u.)
ω (a.u.)
HOMO
LUMO
LUMO+1
$\ell = 2, s = 0$
$\ell = 2, s = 1$
$Z_{\ell,s}$ (a.u.)
R (a.u.)
10
5
0
−5
−10
0
2
4
6
8
10
1.0
0.8
0.6
0.4
0.2
0.0
0.6
0.8
1.0
1.2
1.4

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Article

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Unphysical Discontinuities in *GW* Methods

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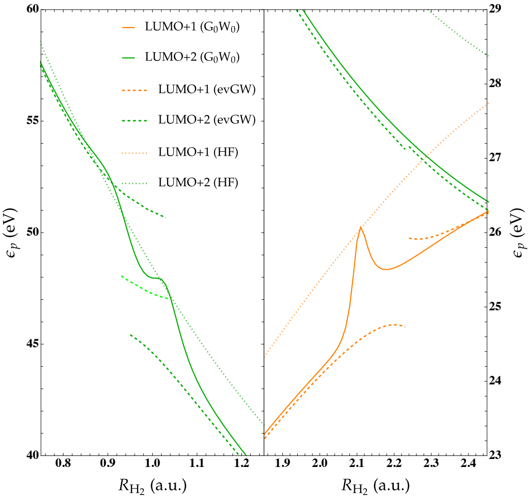
The elephant in the room of GW



(Linearized) quasiparticle equation

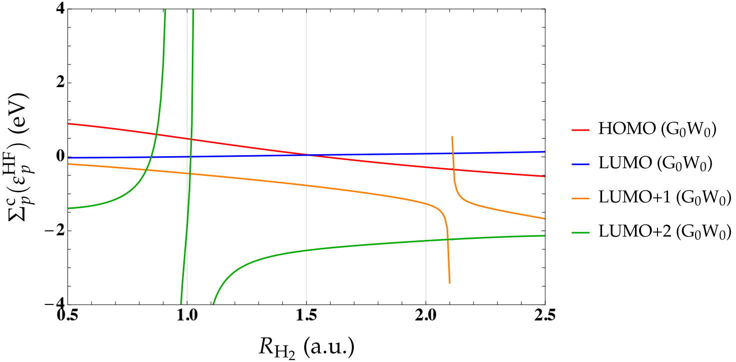
$$\epsilon_p^{G_0 W_0} = \epsilon_p^{\text{HF}} + Z_p(\epsilon_p^{\text{HF}}) \,\text{Re}[\Sigma_p^{\text{c}}(\epsilon_p^{\text{HF}})]$$

Correlation part of the self-energy:

$$\Sigma_p^{\text{c}}(\omega) = 2 \sum_{im} \frac{[pi|m]^2}{\omega - \epsilon_i^{\text{HF}} + \Omega_m^{\text{RPA}} - i\eta} + 2 \sum_{am} \frac{[pa|m]^2}{\omega - \epsilon_a^{\text{HF}} - \Omega_m^{\text{RPA}} + i\eta}$$

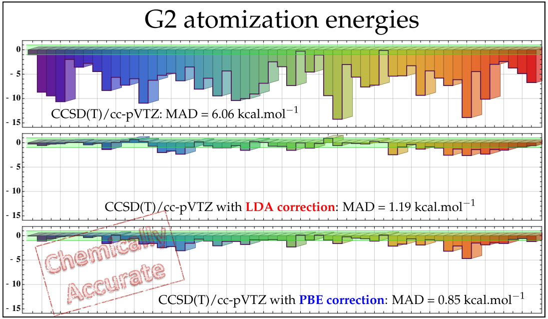
Renormalization factor (or spectral weight):

$$Z_p(\omega) = \left[1 - \frac{\partial \,\text{Re}[\Sigma_p^{\text{c}}(\omega)]}{\partial \omega} \right]^{-1}$$


4
2
0
−2
−4
0.5
1.0
1.5
2.0
2.5
$\Sigma_p^c(\epsilon_p^{HF})$ (eV)
R_{H_2} (a.u.)
HOMO (G_0W_0)
LUMO (G_0W_0)
LUMO+1 (G_0W_0)
LUMO+2 (G_0W_0)

Section 2

Basis set incompleteness correction



THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

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A Density-Based Basis-Set Correction for Wave Function Theory

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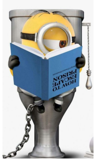
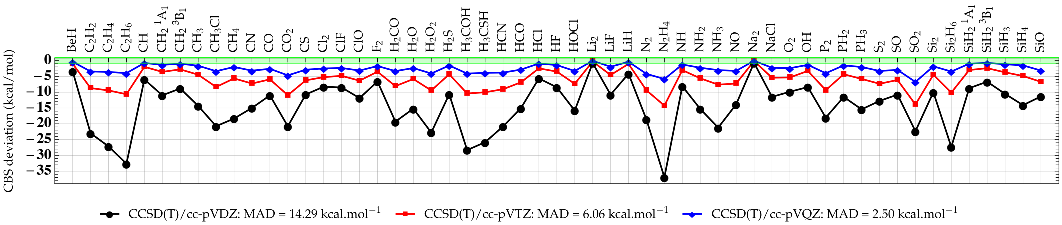
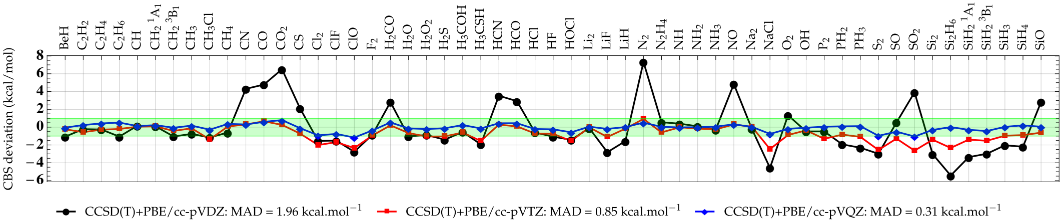


Density-based basis set incompleteness error





Chemically accurate excitation energies with small basis sets

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Emmanuel Giner,[1,a)] Anthony Scemama,[2] Julien Toulouse,[1] and Pierre-François Loos[2,a)]

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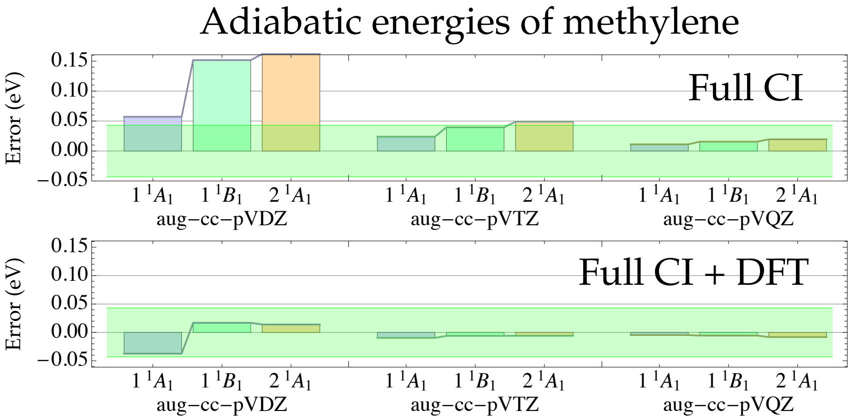
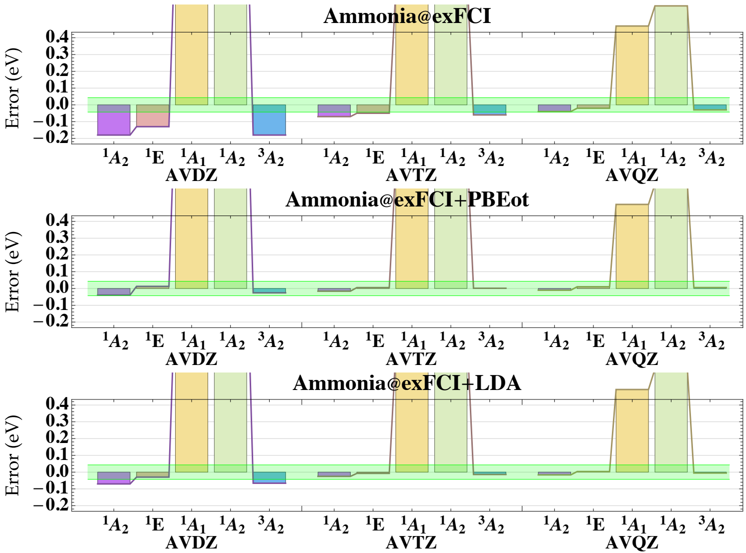


Adiabatic energies of methylene
Full CI
Full CI + DFT
Error (eV)
0.15
0.10
0.05
0.00
−0.05
1 ¹A₁
1 ¹B₁
2 ¹A₁
aug−cc−pVDZ
aug−cc−pVTZ
aug−cc−pVQZ

Density-based basis set incompleteness error



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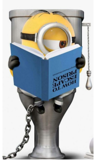
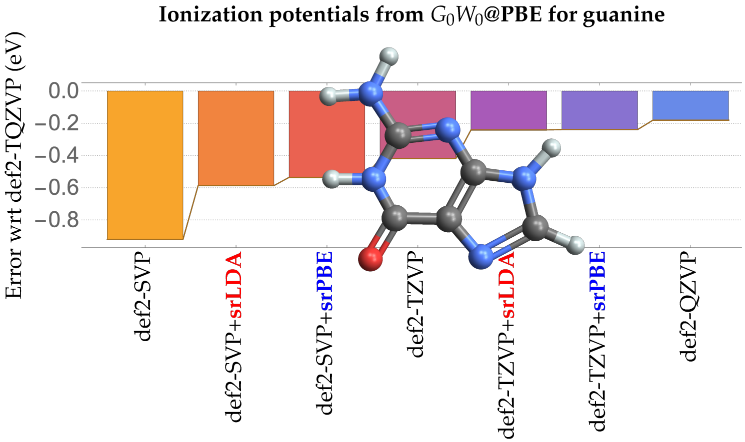
Density-Based Basis-Set Incompleteness Correction for *GW* Methods

Pierre-François Loos,* Barthélémy Pradines, Anthony Scemama, Emmanuel Giner, and Julien Toulouse*

Cite This: *J. Chem. Theory Comput.* 2020, 16, 1018–1028 Read Online

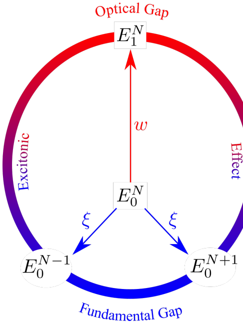





Ionization potentials from G_0W_0@PBE for guanine
Error wrt def2-TQZVP (eV)
0.0
−0.2
−0.4
−0.6
−0.8
def2-SVP
def2-SVP+srLDA
def2-SVP+srPBE
def2-TZVP
def2-TZVP+srLDA
def2-TZVP+srPBE
def2-QZVP

Section 3

Density-functional theory for ensembles




COMING SOON




Ensemble energy:

$$\boxed{E^{\mathbf{w}} = (1 - w_1 - w_2) E^{(0)} + w_1 E^{(1)} + w_2 E^{(2)}}$$

Excitation energies:

$$\frac{\partial E^{\mathbf{w}}}{\partial w_1} = E^{(1)} - E^{(0)} = \Omega^{(1)} \qquad \frac{\partial E^{\mathbf{w}}}{\partial w_2} = E^{(2)} - E^{(0)} = \Omega^{(2)}$$

Ensemble energy in practice:

$$E^{\mathbf{w}} = \min_n \left\{ F^{\mathbf{w}}[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \right\} \qquad F^{\mathbf{w}}[n] = T_s^{\mathbf{w}}[n] + E_{\text{Hxc}}{\mathbf{w}}[n]$$

Derivative discontinuity:

$$\boxed{\frac{\partial E^{\mathbf{w}}}{\partial w_I} = \mathcal{E}_I^{\mathbf{w}} - \mathcal{E}_0^{\mathbf{w}} + \left. \frac{\partial E_{\text{xc}}^{\mathbf{w}}[n]}{\partial w_I} \right|_{n=n^{\mathbf{w}}(\mathbf{r})} \qquad E_{\text{xc}}^{\mathbf{w}}[n] = \int \epsilon_{\text{xc}}^{\mathbf{w}}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r}}$$

Construction of a weight-dependent LDA functional

Three-state ensemble exchange-correlation functional:

$$\tilde{\epsilon}_{xc}^{w_1,w_2}(n) = (1 - w_1 - w_2)\epsilon_{xc}^{(0)}(n) + w_1\epsilon_{xc}^{(1)}(n) + w_2\epsilon_{xc}^{(2)}(n)$$

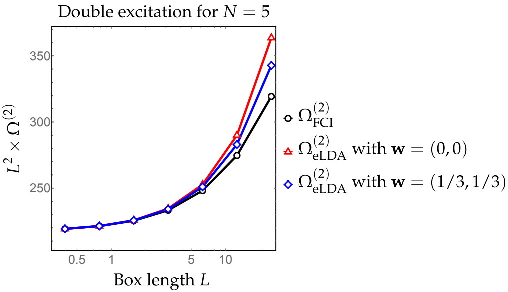
LDA-centered functionals:

$$\bar{\epsilon}_{xc}^{(I)}(n) = \epsilon_{xc}^{(I)}(n) + \epsilon_{xc}^{\text{LDA}}(n) - \epsilon_{xc}^{(0)}(n)$$

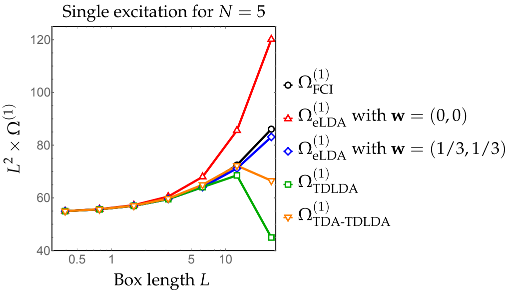
$$\tilde{\epsilon}_{xc}^{w_1,w_2}(n) \to \epsilon_{xc}^{w_1,w_2}(n) = (1 - w_1 - w_2)\bar{\epsilon}_{xc}^{(0)}(n) + w_1\bar{\epsilon}_{xc}^{(1)}(n) + w_2\bar{\epsilon}_{xc}^{(2)}(n)$$

Weight-dependent LDA functional for ensembles "eLDA":

$$\boxed{\epsilon_{xc}^{w_1,w_2}(n) = \epsilon_{xc}^{\text{LDA}}(n) + w_1\left[\epsilon_{xc}^{(1)}(n) - \epsilon_{xc}^{(0)}(n)\right] + w_2\left[\epsilon_{xc}^{(2)}(n) - \epsilon_{xc}^{(0)}(n)\right]}$$



Double excitation for $N = 5$
$L^2 \times \Omega^{(2)}$
250
300
350
0.5
1
5
10
Box length L
$\Omega^{(2)}_{\text{FCI}}$
$\Omega^{(2)}_{\text{eLDA}}$ with $\mathbf{w} = (0, 0)$
$\Omega^{(2)}_{\text{eLDA}}$ with $\mathbf{w} = (1/3, 1/3)$



Single excitation for $N = 5$
$L^2 \times \Omega^{(1)}$
40
60
80
100
120
0.5
1
5
10
Box length L
$\Omega^{(1)}_{\text{FCI}}$
$\Omega^{(1)}_{\text{eLDA}}$ with $\mathbf{w} = (0, 0)$
$\Omega^{(1)}_{\text{eLDA}}$ with $\mathbf{w} = (1/3, 1/3)$
$\Omega^{(1)}_{\text{TDLDA}}$
$\Omega^{(1)}_{\text{TDA-TDLDA}}$

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PT-symmetric electronic structure theory

$\hat{H}\Psi = E\Psi$