Beyond RPA and GW: renormalized second-order perturbation theory for ground-state and excited-state calculations

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In collaboration with
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Thanks to all FHI-aims people
Ground state and excited states of condensed matters

- Ground-state energy $\rightarrow$ structures, interaction strengths, cohesive properties, etc.

- Excitation energies $\rightarrow$ Photoemission spectroscopy, transport properties, etc.

\[ h_n e^- / 0 / 0 \]
State-of-the-art first-principles methods

- **Ground-state energies:**
  Density-functional theory (DFT) with **advanced** exchange-correlation functionals: hybrid functionals, **random-phase approximation (RPA)**, double hybrids.

- **Single-particle excitation energies (self-energy!):**
  \[ \epsilon_s = E(N, 0) - E(N - 1, s) \]  and  \[ \epsilon_t = E(N + 1, t) - E(N, 0) \]
  The **GW** method
State-of-the-art first-principles methods

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The GW method

For certain problems, one even needs to go beyond RPA and GW.

Diagrammatic technique \( \rightarrow \) renormalized 2nd-order perturbation theory (rPT2) to correct RPA and GW.
The Fritz Haber Institute *ab initio* molecular simulations package (FHI-aims)

Local atom-centered basis

\[ \varphi_{i[lm]}(r) = \frac{u_i(r)}{r} Y_{lm}(\Omega) \]

Standard DFT (LDA, GGA)

- all-electron
- periodic, cluster systems on equal footing
- favorable scaling (system size and CPUs)

Beyond standard DFT all based on ”resolution of identity”

- Hartree-Fock, hybrid functionals (PBE0, HSE, B3LYP), MP2, double hybrids, RPA, rPT2
- quasiparticle self-energies: \( GW \), MP2, fully self-consistent \( GW \)


See F. Caruso’ talk
Jacob’s ladder in DFT (John Perdew)

The exchange-correlation functional

<table>
<thead>
<tr>
<th>sophistication</th>
<th>5</th>
<th>unoccupied $\psi_n(r)$, e.g., RPA and its variants</th>
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<tbody>
<tr>
<td>4</td>
<td>occupied $\psi_n(r)$, hybrid functional (e.g., PBE0)</td>
<td></td>
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<tr>
<td>3</td>
<td>$\nabla^2 n(r), \tau(r)$, meta-GGA (e.g., TPSS)</td>
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<td>2</td>
<td>$\nabla n(r)$, GGAs (e.g., PBE)</td>
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<tr>
<td>1</td>
<td>$n(r)$, LDA</td>
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Bohm & Pines (1953); Gell-Mann & Brueckner (1957); Langreth & Perdew (1977); Furche (2001)
The exchange-correlation functional

<table>
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<tr>
<th>Level</th>
<th>Complexity</th>
<th>Functional Type</th>
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<tr>
<td>1</td>
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<td>$n(r)$, LDA</td>
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<tr>
<td>2</td>
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- Level 1-4 are lacking the long-range vdW tails
- RPA and beyond hold promise to describe (nearly) all bonding situations

Bohm & Pines (1953); Gell-Mann & Brueckner (1957); Langreth & Perdew (1977); Furche (2001)
Attractive features of RPA:

- Compatible with exact exchange, including which \((EX+cPRA)\) cancels the self-interaction errors present in the Hartree energy. (not self-correlation free though)

- Automatic and seamless inclusion of van der Waals interactions

- No intrinsic limitations \(\implies\) applicable to (bio)molecules, insulators & metals, surfaces and interfaces, etc.

- Static correlation is (partly) captured (e.g, \(H_2\) bond breaking well described)

RPA calculations in practice

In practical calculations, RPA is done perturbatively on a LDA/GGA reference (e.g., RPA@PBE)

The “standard” RPA scheme:

\[
E^{\text{RPA@PBE}} = E^{\text{PBE}} - E^{\text{xc}} + \left( E_x^{\text{exact}} + E^\text{RPA}_c \right) @\text{PBE}
\]
\[
= \left( E_{\text{kin}} + E_{\text{ext}} + E_{\text{Hartree}} + E_x^{\text{exact}} + E^\text{RPA}_c \right) @\text{PBE}
\]
\[
= E^{\text{EX@PBE}} + E^\text{RPA@PBE}_c
\]

- \( E^{\text{EX@PBE}} \): non-self-consistent Hartree-Fock energy (exchange-only total energy) evaluated with PBE orbitals.

- \( E^\text{RPA@PBE}_c \): RPA correlation energy evaluated with PBE orbitals.
RPA applied to surface adsorption problem

“CO adsorption puzzle”

\[ E_{\text{ads}} \] (eV)

- LDA
- PBE
- PBE0
- RPA@PBE


And also

The $\alpha - \gamma$ phase transition of Ce (M. Cacadei et al, PRL, in print)
However, standard RPA shows a general tendency to underbind.

\[ \text{Mean error (eV)} \]

- PBE
- RPA@PBE
- PBE0

Overbinding

Insulating crystals


RPA for describing the van der Waals interactions

![Graph showing binding energy vs. bond length]


- Correct asymptotic behavior, crucial for large molecules
- Underbinding around the equilibrium distance
Attempts for going beyond RPA

- “RPA+” and “RPA++”: correct RPA using local and/or non-local density functional correlations.

- Range-separated RPA: only the long-range part of RPA is incorporated.

- SOSEX: complement RPA with second-order screened exchange.

- SE correction: add a single-excitation (SE) contribution to cRPA.
The second-order screened exchange correction to RPA

Diagrammatic (Goldstone) representation (originally motivated from the coupled cluster context)

$$E_{c}^{\text{RPA+SOSEX}} = \begin{array}{c}
\quad 
+ \\
+ \\
= \\
\end{array} \begin{array}{c}
\text{2nd-order} \\
\text{3rd-order} \\
\end{array}$$

Arising from the anti-symmetric nature of many-body wave function

RPA+SOSEX is one-electron self-correlation free

SOSEX correction alleviates the underbinding problem of RPA!
The concept of single excitation (SE) correction

Rayleigh-Schrödinger perturbation theory:

\[ \hat{H} = \hat{H}^0 + \hat{H}' \]

Ground-state energy: \( E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \cdots \)

- zeroth-order: \( E_0^{(0)} = \langle \Phi_0 | \hat{H}^0 | \Phi_0 \rangle \)
- 1st order: \( E_0^{(1)} = \langle \Phi_0 | \hat{H}' | \Phi_0 \rangle \)
- 2nd order:
  \[
  E_0^{(2)} = \sum_{n \neq 0} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} = \sum_{i,a} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_{i,a} \rangle|^2}{E_0^{(0)} - E_{i,a}^{(0)}} + \sum_{ij,ab} \frac{|\langle \Phi_0 | \hat{H}' | \Phi_{ij,ab} \rangle|^2}{E_0^{(0)} - E_{ij,ab}^{(0)}}
  \]
  \[ \text{Single excitations} \quad E_c^{SE} \]
  \[ \text{Double excitations} \quad \text{MP2} \]

SE accounts for the orbital relaxation effect.
Performance of RPA+SE for $\text{Ar}_2$

Performance of RPA+SE for atomization energies

The concept of Renormalized 2nd-order Perturbation Theory (rPT2)

\[ E_{c}^{RPA+SOSEX+rSE} = \left( = \text{RPA}\right) \]

\[ = \left( = \text{SOSEX}\right) \]

\[ = \left( = \text{rSE}\right) \]

( = 2PT)

“rPT2” = “RPA+SOSEX+rSE”
Performance of rPT2 for $\text{Ar}_2$

![Graph showing binding energy vs. bond length for Ar₂](image)

- PBE
- RPA@PBE
- rPT2
- Reference
- RPA+SE

Atomization energies within rPT2

Performance of rPT2 for non-covalent interactions
Interaction energies for S22 and S66 sets

![Bar chart showing mean absolute percentage error for different interactions]

<table>
<thead>
<tr>
<th>Bonding type</th>
<th>hydrogen dispersion</th>
<th>mixed</th>
</tr>
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<tbody>
<tr>
<td>S22 [1]</td>
<td>7</td>
<td>8</td>
</tr>
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</table>

Performance of rPT2 for chemical reaction barrier heights

38 hydrogen-transfer barrier heights (HTBT-38) and 38 non-hydrogen-transfer barrier heights (NHTBH-38)

Mean absolute error (kcal/mol)

Part II:

Second-order screened exchange correction to the $GW$ self-energy
The \textit{GW} method

- Quasiparticle equation for interacting many-electron systems

\[ H_0 \psi_{n}^{\text{QP}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_{n}^{\text{QP}}) \psi_{n}^{\text{QP}}(\mathbf{r}') = \varepsilon_{n}^{\text{QP}} \psi_{n}^{\text{QP}}(\mathbf{r}) \]

- \textit{GW} approximation

\[ \Sigma(\mathbf{r}, \mathbf{r}', i\omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', i\omega + i\omega') W(\mathbf{r}, \mathbf{r}', i\omega') \]

\[ W = v/(1 - \chi v) = v + v\chi v + \cdots \]

\[ \text{Feynman diagram} \]

\[ \text{= - - - - - + - - - - + ...} \]

Photoemission spectra of benzene

![Graph showing photoemission spectra of benzene with labels for different energy levels and intensities.](image)

Exp. PES

$G_0 W_0 @PBE$

$G_0 W_0 @PBE0$

$G_0 W_0 @HF$

$(G_0 W_0 +2OX)@PBE$

Energy (eV)

Intensity (arbitrary unit)

N. Marom et al., in preparation.
Diagrammatic representation of the screened 2nd-order exchange self-energy

Screened second-order exchange $\Sigma_{c}^{\text{SOSEX}}$:
(to reduce the "self-correlation")

$\Sigma_{x}^{\text{HF}}$ and $\Sigma_{c}^{\text{GW}}$: antisymmetrization
Photoemission spectra of benzene

Exp. PES
$G_0W_0 + \text{SOSEX}$

$G_0W_0 @ \text{PBE}$

$G_0W_0 @ \text{PBE0}$

$G_0W_0 @ \text{HF}$

$(G_0W_0 + 2\text{OX}) @ \text{PBE}$

$e_1g\pi$

$e_2g\sigma$

$a_{2u}\pi$

Intensity (arbitrary unit)

Energy (eV)

-20 -18 -16 -14 -12 -10 -8
Error analysis for 50 atoms and molecules

- $G_0W_0@PBE$: ME = -0.49 eV, MAE = 0.53 eV
- $G_0W_0@PBE0$: ME = -0.15 eV, MAE = 0.25 eV
- $G_0W_0@HF$: ME = 0.41 eV, MAE = 0.52 eV
- $(G_0W_0 + SOSEX)@PBE$: ME = -0.01 eV, MAE = 0.25 eV
Some final remarks

- Is there a single-excitation contribution to the self-energy?

- Screened second-order exchange versus second-order self-energy in terms of $W$

Diagram: Two diagrams representing improper (reducible) self-energy and a comparison between screened second-order exchange and second-order self-energy in terms of $W$. Denoted by $X$. 