VASP6: total energies beyond DFT

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Outline

• Beyond DFT
  • The need to go beyond DFT
  • HF/DFT hybrid functionals
  • The Random-Phase-Approximation

• $O(N^3)$ implementation of the RPA
  • Cubic-scaling RPA total energies
  • Minimax frequency and time integration
  • Cubic-scaling RPA quasi-particles

• Forces in the RPA
• Total energy differences with "chemical accuracy"
  (1 kcal/mol ≈ 40 meV/atom):
  Atomization-, formation energies, reaction barriers, etc
• Van der Waals interactions

• Bandstructure of metals and largish gap systems, and some problematic cases inbetween
CO adsorption on d-metal surfaces


- This error is relatively large. Best DFT/PBE calculations:
  - CO@Cu(111): $-170$ meV
  - CO@Rh(111): $-40$ meV
  - CO@Pt(111): $-100$ meV

- CO HOMO-LUMO gap too small in DFT:
## CO adsorption on d-metal surfaces

<table>
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<th>CO @</th>
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<th>fcc</th>
<th>hcp</th>
<th>Δ</th>
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<td>1.43-1.71</td>
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</table>

(All energies in eV)

A. Stroppa et al., PRB 76, 195440 (2007); A. Stroppa and G. Kresse, NJP 10, 063020 (2008).
Hybrid functionals reduce the tendency to stabilize adsorption at the hollow site w.r.t. the top site.

reduced CO $2\pi^*$ – metal-$d$ interaction

- DFT does well for the metallic surface, but not for the CO: $2\pi^*$ (LUMO) too close to the Fermi level.
- HSE does well for the CO, but not for the surface: $d$-metal bandwidth too large.

The Random-Phase-Approximation: GW and ACFDT

- Quasiparticles from GW: “electronic structure” in the RPA.
- Total energies from the ACFDT in the RPA.
- Are the above related?
One-electron/QP picture

DFT: Kohn-Sham eq.

\[ \left( -\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}[\rho](\mathbf{r}) \right) \psi_{nk}(\mathbf{r}) = \epsilon_{nk} \psi_{nk}(\mathbf{r}) \]

DFT-HF hybrid functionals: Roothaan eq.

\[ \left( -\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \right) \psi_{nk}(\mathbf{r}) + \int V_{\text{X}}[\{\psi_{o}\}](\mathbf{r},\mathbf{r}') \psi_{nk}(\mathbf{r}')d\mathbf{r}' = \epsilon_{nk} \psi_{nk}(\mathbf{r}) \]

GW: quasi-particle eq.

\[ \left( -\frac{1}{2}\Delta + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \right) \psi_{nk}(\mathbf{r}) + \int \Sigma[\{\psi, E\}](\mathbf{r}, \mathbf{r}', E_{nk}) \psi_{nk}(\mathbf{r}')d\mathbf{r}' = E_{nk} \psi_{nk}(\mathbf{r}) \]
The quasi-particle equation:
\[
\left(-\frac{1}{2}\Delta + V_{\text{ext}}(r) + V_H(r)\right)\psi_{nk}(r) + \int \Sigma(r, r', E_{nk})\psi_{nk}(r')dr' = E_{nk}\psi_{nk}(r)
\]

The “self-energy is given by:
\[
\Sigma = iGW
\]

or more explicitly
\[
\Sigma(r, r', E) = \frac{i}{2\pi} \int_{-\infty}^{\infty} d\omega \sum_{n} \frac{\psi_{n}(r)\psi_{n}^{*}(r')}{\omega - E - E_{n} + i\eta \text{sgn}(E_{n} - E_{\text{fermi}})}
\]

\[
\times e^{2} \int d\mathbf{r}' \frac{\varepsilon^{-1}(r, r', \omega)}{|\mathbf{r}' - \mathbf{r}|}
\]

Compare to Fock-exchange:
\[
V_{X}(r, r') = -\sum_{n}^{\text{occ.}} \psi_{n}(r)\psi_{n}^{*}(r') \times \frac{e^{2}}{|r - r'|}
\]
The Green’s function: physical interpretation

The Green’s function $G(r, r', t - t')$ describes the propagation of a particle from $(r, t)$ to $(r', t')$: i.e., provided we have particle at position $r$ at time $t$, $G(r, r', t - t')$ is the chance of finding it at position $r'$ at time $t'$.

$$G_0(r, r', \omega) = \sum_n^{\text{all}} \frac{\psi_n^*(r)\psi_n(r')}{\omega - \epsilon_n + i\eta \text{sgn}(\epsilon_n - \mu)}$$

- Particle propagator: $G_0(1, 2) = G_o(r_1, r_2, t_2 - t_1)$ for $t_2 > t_1$:

  $$(r_1, t_1) = 1 \quad (r_2, t_2) = 2 \quad G_0(1, 2) = \sum_n^{\text{vir.}} \psi_n(r_1)^*\psi_n(r_2)e^{-i(\epsilon_n - \mu)(t_2 - t_1)}$$

- Hole propagator: $G_0(1, 2)$ for $t_1 > t_2$:

  $$(r_2, t_2) = 2 \quad (r_1, t_1) = 1 \quad G_0(1, 2) = \sum_n^{\text{occ.}} \psi_n^*(r_1)\psi_n(r_2)e^{-i(\epsilon_n - \mu)(t_1 - t_2)}$$
In the RPA, the screened Coulomb interaction is computed from $\chi^0$ as:

$$\chi^0(r, r', \omega) := \frac{\partial \rho_{\text{ind}}(r, \omega)}{\partial v_{\text{eff}}(r', \omega)}$$

Key: the “irreducible polarizability in the independent particle picture” $\chi^0$ (or $\chi^{KS}$):

$$W = \nu + \nu \chi^0 \nu + \nu \chi^0 \nu \chi^0 \nu + \nu \chi^0 \nu \chi^0 \nu + \ldots = \nu \left(1 - \chi^0 \nu\right)^{-1}$$

1. The bare Coulomb interaction between two particles

2. The electronic environment reacts to the field generated by a particle: induced change in the density $\chi^0 \nu$, that gives rise to a change in the Hartree potential: $\nu \chi^0 \nu$.

3. The electrons react to the induced change in the potential: additional change in the density, $\chi^0 \nu \chi^0 \nu$, and corresponding change in the Hartree potential: $\nu \chi^0 \nu \chi^0 \nu$.

and so on, and so on ...

$$W = \epsilon^{-1} \nu \quad \epsilon^{-1} = 1 + \nu \chi \quad \chi = \chi^0 + \chi^0 \nu \chi$$

geometrical series
The “irreducible polarizability in the independent particle picture” $\chi^0$ (or $\chi^{KS}$):

$$\chi^0(r, r', \omega) := \frac{\partial \rho_{\text{ind}}(r, \omega)}{\partial v_{\text{eff}}(r', \omega)}$$

Adler and Wiser derived expressions for $\chi^0$

$$\chi^0(r_1, r_2, \omega) = \sum_{\text{occ.}} \sum_{\text{virt.}} \frac{\langle \psi_a | r_1 | \psi_i \rangle \langle \psi_i | r_2 | \psi_a \rangle}{\epsilon_i - \epsilon_a - \omega} + \sum_{\text{occ.}} \sum_{\text{virt.}} \frac{\langle \psi_i | r_1 | \psi_a \rangle \langle \psi_a | r_2 | \psi_i \rangle}{\epsilon_a - \epsilon_i - \omega}$$

Or in terms of Green’s functions (propagators):

$$\chi^0(r_1, t_1, r_2, t_2) = \chi(1, 2) = -G_0(1, 2)G_0(2, 1)$$

$$W = V + V \chi_0 V + V \chi_0 V \chi_0 V + \ldots$$
GW in the RPA
RPA total energies (ACFDT)

The “RPA” total energy is given by:
\[
E[n] = T_{KS}[[\psi_i]] + E_H[n] + E_X[[\psi_i]] + E_{\text{ion-el}}[n] + E_c
\]

with the RPA correlation energy
\[
E_c = \sum_q \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}\{\ln[1 - \chi_0(q, i\omega)\nu] + \chi_0(q, i\omega)\nu\}
\]

and the Independent-Particle polarizability:
\[
\chi^0(r, r', \omega) := \frac{\partial \rho_{\text{ind}}(r, \omega)}{\partial \nu_{\text{eff}}(r', \omega)}
\]

\[
\chi_{G,G'}^0(q, \omega) = \frac{1}{\Omega} \sum_{nn'k} 2w_k (f_{n'k+q} - f_{n'k})
\]
\[
\times \frac{\langle \psi_{n'k+q} | e^{i(q+G)r} | \psi_{nk} \rangle \langle \psi_{nk} | e^{-i(q+G')r'} | \psi_{n'k+q} \rangle}{\epsilon_{n'k+q} - \epsilon_{nk} - \omega - i\eta}
\]

\[
\ln(1 - \chi_0\nu) + \chi_0\nu = -\frac{\text{Tr}[\chi_0\nu\chi_0\nu]}{2} - \frac{\text{Tr}[\chi_0\nu\chi_0\nu\chi_0\nu]}{3} - \frac{\text{Tr}[\chi_0\nu\chi_0\nu\chi_0\nu\chi_0\nu]}{4} \ldots
\]
In terms of diagrams

\[
\ln(1 - \chi_0 v) + \chi_0 v = - \frac{\text{Tr}[\chi_0 v \chi_0 v]}{2} - \frac{\text{Tr}[\chi_0 v \chi_0 v \chi_0 v]}{3} - \frac{\text{Tr}[\chi_0 v \chi_0 v \chi_0 v \chi_0 v]}{4} + \ldots
\]

The derivate w.r.t. \( G \) yields GW!

\[
\frac{\partial E_c}{\partial G} = \Sigma
\]
RPA: lattice constants
J. Harl et al., PRB 81, 115126 (2010)

Deviations w.r.t. experiment (corrected for zero-point vibrations)

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<thead>
<tr>
<th></th>
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<th>MARE</th>
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<tr>
<td>PBE</td>
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<td>MP2</td>
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<tr>
<td>RPA</td>
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</table>

(in %)
RPA: noble gas solids
J. Harl and G. Kresse, PRB 77, 045136 (2008)

Correlation energy (eV) vs. volume (Å³) for Neon, Argon, and Krypton.

Cohesive Energy [meV] vs. Volume [Å³] for Argon with LDA, PBE, ACFDT, and MP2.

<table>
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<th>RPA(PBE)</th>
<th>Exp.</th>
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<td>Ne</td>
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<td>53</td>
<td>47</td>
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<tr>
<td>Ar</td>
<td>512</td>
<td>484</td>
<td>455</td>
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<tr>
<td>Kr</td>
<td>1030</td>
<td>980</td>
<td>895</td>
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</table>

C₆ coefficients

RPA: noble gas solids
J. Harl and G. Kresse, PRB 77, 045136 (2008)
Graphite vs. Diamond

1/d^4 behavior at short distances

<table>
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<tr>
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<tr>
<td>d(Å)</td>
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<td>3.34</td>
<td>3.34</td>
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<td>C_{33}</td>
<td>36</td>
<td>36-40</td>
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<tr>
<td>E(meV)</td>
<td>56</td>
<td>48</td>
<td>43-50</td>
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</tbody>
</table>

J. Harl, G. Kresse, PRL 103, 056401 (2009).
RPA: heats of formation
J. Harl and G. Kresse, PRL 103, 056401 (2009)

Heats of formation w.r.t. normal state at ambient conditions (in kJ/mol)

Example: Mg(bulk metal) + H\textsubscript{2} → MgH\textsubscript{2}

<table>
<thead>
<tr>
<th></th>
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<td>SiC</td>
<td>51</td>
<td>69</td>
<td>64</td>
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RPA: CO @ Pt(111) and Rh(111)

RPA:
• increases surface energy and
• decreases adsorption energy

FIG. 1: Atop CO adsorption and surface energies for Pt(111) and Rh(111). (a) Considered CO adsorption geometries for a $(2 \times 2)$ surface cell. Semi-local functionals predict CO to adsorb in the fcc hollow site coordinated to three metal atoms on Pt and Rh, whereas experiments unequivocally show adsorption atop a metal atom. (b) Atop adsorption energies versus surface energies for Pt(111) and Rh(111). Various semi-local functionals were used: AM05$^{10}$, PBEsol$^{11}$, PBE$^8$, rPBE$^{12}$ and BLYP$^{13}$, in order of increasing gradient corrections. Furthermore the hybrid functional HSE$^{18}$ based on the PBE functional was used.
• DFT does well for the metallic surface, but not for the CO: $2\pi^*$ (LUMO) too close to the Fermi level.

• HSE does well for the CO, but not for the surface: $d$-metal bandwidth too large.

• GW gives a good description of both the metallic surface as well as of the CO $2\pi^*$ (LUMO). The CO $5\sigma$ and $1\pi$ are slightly underbound.

RPA:

- Right site preference
- Good adsorption energies
- Excellent lattice constants
- Good surface energies
As shown by Adler and Wiser, the IP polarizability \( \chi^0 \) can be straightforwardly calculated from \( \{\psi, \epsilon\} \):

\[
\chi^0_{G,G'}(q, \omega) = \frac{1}{\Omega} \sum_{nn'kk} 2w_k (f_{n'k+q} - f_{n'k}) \times \frac{\langle \psi_{n'k+q} | e^{i(q+G)r} | \psi_{nk} \rangle \langle \psi_{nk} | e^{-i(q+G')r'} | \psi_{n'k+q} \rangle}{\epsilon_{n'k+q} - \epsilon_{nk} - \omega - i\eta}
\]

Expensive: this scales as \( N^4 \)!
Evaluate the Green's function in “imaginary” time:

\[ G(r, r', i\tau) = \sum_n \psi_n(r)\psi^*_n(r')e^{-\epsilon_n\tau} \]

and the polarizability as:

\[ \chi^0(r, r', i\tau) = -G(r, r', i\tau)G(r, r', -i\tau) \]

Followed by a cosine-transform:

\[ \chi^0(r, r', i\tau) \xrightarrow{\text{CT}} \chi^0(r, r', i\omega) \]

Now the worst scaling steps are the evaluation of the Greens function \(N^3\), and

\[ E_c = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}\{\ln[1 - \chi_0(i\omega)\nu] + \chi_0(i\omega)\nu\} \]

(which scales as \(N^3\) due to the diagonalization involved in evaluating the “\(\ln\)”).

The evaluation of the polarizability scales quadratically \(N^2\)!

But storing \(G\) and \(\chi\) is expensive! \(\rightarrow\) we need small sets of cleverly chosen “\(\tau\)” and “\(\omega\)”
The “minimax” fit

Express a function $f(x)$ in a basis of $N$ functions $\{\varphi(\alpha_i, x) | i = 1, \ldots, N\}$, such that the error:

$$\eta(\vec{\alpha}, \vec{\beta}, x) = f(x) - \sum_i \beta_i \varphi(\alpha_i, x)$$

is “as small as possible”.

Choose $\{(\alpha_i, \beta_i) | i = 1, \ldots, N\}$ so that the maximum error:

$$||\eta||_\infty := \max_{a \leq x \leq b} |\eta(\vec{\alpha}, \vec{\beta}, x)|$$

is minimized.

This solution, $\{(\alpha_i^*, \beta_i^*) | i = 1, \ldots, N\}$, is the so-called ”minimax” solution.
The “minimax” frequency grid
M. Kaltak, J. Klimeš, and G. Kresse, JCTC 10, 2498 (2014)

The IP polarizability can be written as (Adler&Wiser):

$$\chi(i \omega) = \sum_{\mu} \chi_{\mu} \phi(\omega, x_{\mu})$$

where

$$\phi(\omega, x) = \frac{2x}{x^2 + \omega^2}$$

Determine a frequency grid and quadrature weights by expressing the “2nd-order direct Møller-Plesset energy”

$$E_c^{(2)} = -\frac{1}{8\pi} \int_{-\infty}^{\infty} d\omega \{\chi(i \omega) \nu\}^2$$

in the basis \(\{\phi(\omega_i, x) \} \) in the minimax sense:

\[
\{(\gamma_k^*, \omega_k^*) \mid k = 1, \ldots, N\} \quad \eta(\vec{\gamma}, \vec{\omega}, x) = \frac{1}{x} - \frac{1}{\pi} \sum_{k=1}^{N} \gamma_k \phi^2(\omega_k, x) \quad E_g \leq x \leq \max(\epsilon_a - \epsilon_i)
\]

$$E_c^{(2)} = -\frac{1}{8\pi} \int_{-\infty}^{\infty} d\omega \{\chi(i \omega) \nu\}^2 \quad \Rightarrow \quad E_c^{(2)} \approx -\frac{1}{8\pi} \sum_{k=1}^{N} \gamma_k^* \{\chi(i \omega_k^*) \nu\}^2$$
The “minimax” time grid
M. Kaltak, J. Klimeš, and G. Kresse, JCTC 10, 2498 (2014)

Alternatively the IP polarizability can be written as:

\[ \hat{\chi}(i\tau) = \sum_{\mu} \chi_\mu \hat{\phi}(\tau, x_\mu) \]

where \( \hat{\phi}(\tau, x) = e^{-x|\tau|} \)

Determine a frequency grid and quadrature weights by expressing the “2nd-order direct Møller-Plesset energy”

\[ E^{(2)}_c = -\frac{1}{4} \int_{-\infty}^{\infty} d\tau \{ \hat{\chi}(i\tau)\nu \}^2 \]

in the basis \( \{ \hat{\phi}(\tau_i, x)|i = 1, \ldots, N \} \) in the minimax sense:

\[
\{(\sigma^*_k, \tau^*_k)|k = 1, \ldots, N\} \quad \hat{\eta}(\vec{\sigma}, \vec{\tau}, x) = \frac{1}{2x} - \sum_{k=1}^{N} \sigma_k \hat{\phi}^2(\tau_k, x) \quad E_g \leq x \leq \max(\epsilon_a - \epsilon_i)
\]

\[ E^{(2)}_c = -\frac{1}{4} \int_{-\infty}^{\infty} d\tau \{ \hat{\chi}(i\tau)\nu \}^2 \quad \Rightarrow E^{(2)}_c \approx -\frac{1}{4} \sum_{k=1}^{N} \sigma^*_k \{ \hat{\chi}(i\tau^*_k)\nu \}^2 \]
The non-uniform cosine transform
M. Kaltak, J. Klimeš, and G. Kresse, JCTC 10, 2498 (2014)

The cosine transform of $\chi(i\omega) \leftrightarrow \chi(i\tau)$:

$$\chi(i\omega) = 2 \int_{0}^{\infty} d\tau \hat{\chi}(i\tau) \cos(\omega\tau) \quad \hat{\chi}(i\tau) = \frac{1}{\pi} \int_{0}^{\infty} d\omega \chi(i\omega) \cos(\omega\tau)$$

is reformulated on the minimax frequency and time grids as

$$\chi(i\omega_k) = \sum_{l=1}^{N} a_{kl} \hat{\chi}(i\tau_l)$$

$$a_{kl} = w_{kl} \cos(\omega_k^* \tau_l^*)$$

where the coefficients $w_{kl}$ are the minimax solution to the following fitting problem:

$$\eta^c(\vec{w}_k, x) = \phi(\omega_k^*, x) - \sum_{l=1}^{N} w_{kl} \cos(\omega_k^* \tau_l^*) \hat{\phi}(\tau_l^*, x) \quad \text{minimax fit} \quad \{w_{kl}|k, l = 1, .., N\}$$

for fixed $\{\omega_k^*\}$ and $\{\tau_l^*\}$, and for $E_g \leq x \leq \max(\epsilon_a - \epsilon_i)$. 
How good are the grids: ZnO and Si

- $N^4$ RPA calculations entirely in frequency
- $N^2$ calculation of polarizability in time, then transformation to frequency (200 atoms on 200 cores in about one hour)

M. Kaltak, J. Klimeš, and G. Kresse, JCTC 10, 2498 (2014); PRB 90, 054115 (2014).
New RPA code (VASP6):

- Scales linearly in the number of k-points (as DFT), instead of quadratically as for conventional RPA and hybrid functionals
- Scales cubically in system size (as DFT).

Prefactors are much larger than in DFT, but calculations for 200 atoms take less than 1 hour (128 cores)
## Defect formation energies in Si

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<th></th>
<th>PBE</th>
<th>HSE</th>
<th>HSE(+vdW)</th>
<th>QMC</th>
<th>RPA</th>
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<tr>
<td>Dumbbell X</td>
<td>3.56</td>
<td>4.43</td>
<td>4.41</td>
<td>4.4(1)</td>
<td>4.28</td>
</tr>
<tr>
<td>Hollow H</td>
<td>3.62</td>
<td>4.49</td>
<td>4.40</td>
<td>4.7(1)</td>
<td>4.44</td>
</tr>
<tr>
<td>Tetragonal T</td>
<td>3.79</td>
<td>4.74</td>
<td>4.51</td>
<td>5.1(1)</td>
<td>4.93</td>
</tr>
<tr>
<td>Vacancy</td>
<td>3.65</td>
<td>4.19</td>
<td>4.38</td>
<td></td>
<td>4.40</td>
</tr>
</tbody>
</table>


RPA total energy calculation: flow chart

DFT groundstate
- EDIFF = 1E-8
- ISMEAR = 0 ; SIGMA = 0.1
- NBANDS = \lteq maximum # of plane waves
- ALGO = Exact ; NELM = 1
- ISMEAR = 0 ; SIGMA = 0.1
- LOPTICS = .TRUE.  [ ; LPEAD = .TRUE. ]

DFT virtual orbitals
- ALGO = Eigenval ; NELM = 1
- LWAVE = .FALSE.
- LHFCALC = .TRUE. ; AEXX= 1.0
- ISMEAR = 0 ; SIGMA = 0.1

HF energy

RPA energy
- NBANDS = \lteq maximum # of plane waves
- ALGO = RPAR | ACFDTR
- NOMEGA = 12-16
- [ PRECFOCK = Normal ]
... or all in one go!

When one does **not** specify **NBANDS**, **VASP** will run all consecutive steps in one go:

- **EDIFF** = 1E-8
- **ISMÉAR** = 0 ; **SIGMA** = 0.1
- **LOPTICS** = .TRUE. ; **LPEAD** = .TRUE.
- **ALGO** = **RPAR** | **ACFDTR**
- **NOMEGA** = 12-16

[ **PRECFOCK** = Normal ]

[ **NBANDSEXACT** = # of bands in G ]

In this case the number of bands used to compute the Greens function is specified by means of the **NBANDSEXACT** tag (optional).
An example: SiC

INCAR:

ALGO = ACFDTR
NOMEGA = 16
NBANDSEXACT = 120
PREFCOCK = NORMAL

LOPTICS = .TRUE. ; LPEAD = .TRUE.

ISMEAR = 0 ; SIGMA = 0.05
EDIFF = 1E-8

LWAVE = .FALSE.

KPOINTS:

Automatically generated mesh
0
Gamma
3 3 3
0 0 0

POSCAR:

SiC
4.35
0.5 0.5 0.0
0.0 0.5 0.5
0.5 0.0 0.5
1 1
cart
0.00 0.00 0.00
0.25 0.25 0.25
The GW potentials: *-_GW POTCAR files

\[
\Delta(PAW)_{V_{\text{VSP}}} = 0.4 \text{ meV/atom}
\]
running 8 mpi-ranks, with 1 threads/rank
distrk: each k-point on 8 cores, 1 groups
distr: one band on 1 cores, 8 groups
using from now: INCAR
vasp.6.1.2 22Jul20 (build Jul 22 2020 23:58:52) complex

POSCAR found: 2 types and 2 ions
scaLAPACK will be used
LDA part: xc-table for Pade appr. of Perdew
POSCAR, INCAR and KPOINTS ok, starting setup

“DFT groundstate calculation”

<table>
<thead>
<tr>
<th>N</th>
<th>E</th>
<th>dE</th>
<th>d eps</th>
<th>ncg</th>
<th>rms</th>
<th>rms(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.807695689957E+00</td>
<td>-0.80770E+00</td>
<td>-0.25358E+03</td>
<td>80</td>
<td>0.517E+02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-0.160589369121E+02</td>
<td>-0.15251E+02</td>
<td>-0.12187E+02</td>
<td>80</td>
<td>0.986E+01</td>
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<tr>
<td>3</td>
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<td>-0.58688E+00</td>
<td>-0.58688E+00</td>
<td>96</td>
<td>0.179E+01</td>
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<td>4</td>
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<td>-0.17420E-02</td>
<td>-0.17420E-02</td>
<td>64</td>
<td>0.947E-01</td>
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<tr>
<td>5</td>
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<td>-0.21554E-04</td>
<td>-0.21554E-04</td>
<td>104</td>
<td>0.120E-01</td>
<td>0.992E+00</td>
</tr>
<tr>
<td>6</td>
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<td>-0.80384E+00</td>
<td>96</td>
<td>0.241E+01</td>
<td>0.883E+00</td>
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<tr>
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<td>-0.37382E-01</td>
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<td>0.483E+00</td>
<td>0.577E+00</td>
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<tr>
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<td>-0.145238445286E+02</td>
<td>0.10531E-01</td>
<td>-0.25946E-02</td>
<td>80</td>
<td>0.163E+00</td>
<td>0.429E-01</td>
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<tr>
<td>9</td>
<td>-0.145238173443E+02</td>
<td>0.27184E-04</td>
<td>-0.60800E-04</td>
<td>96</td>
<td>0.212E-01</td>
<td>0.972E-02</td>
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<tr>
<td>10</td>
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<td>-0.20754E-03</td>
<td>-0.27113E-04</td>
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<td>0.148E-01</td>
<td>0.118E-02</td>
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<tr>
<td>11</td>
<td>-0.145240278179E+02</td>
<td>-0.29356E-05</td>
<td>-0.22309E-05</td>
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<td>0.467E-02</td>
<td>0.104E-02</td>
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<tr>
<td>12</td>
<td>-0.145240279045E+02</td>
<td>-0.86635E-07</td>
<td>-0.18940E-06</td>
<td>80</td>
<td>0.143E-02</td>
<td>0.134E-03</td>
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<tr>
<td>13</td>
<td>-0.145240279035E+02</td>
<td>0.10211E-08</td>
<td>-0.32364E-08</td>
<td>88</td>
<td>0.170E-03</td>
<td></td>
</tr>
</tbody>
</table>

The Fermi energy was updated, please check that it is located mid-gap
values below the HOMO (VB) or above the LUMO (CB) will cause erroneous energies
E-fermi: 9.6656

“Exact diagonalization and LOPTICS step”

optical routines
imaginary and real dielectric function
direction 1
direction 2
direction 3
stdout (cont.): set up “minimax” grids

| responsefunction array rank= 120 |

| NTAUPAR set to 8 based on available memory per rank (MAXMEM= 2710 MB) |

set NWRITE>2 for more details about minimax calculation
number of imaginary grid points requested: 16
number of distinct grids requested: 4
quadrature errors minimized for energies in [ 0.250E+01, 0.186E+03 ]
time grid (T=0) determined with error: 0.6315E-12
fermionic grid (T=0, re) determined with error: 0.1995E-11
time grid (T=0, re) determined with error: 0.1995E-11
fermionic grid (T=0, im) determined with error: 0.2003E-11

<table>
<thead>
<tr>
<th>bosonic grid (re): 0.1995E-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3979</td>
</tr>
<tr>
<td>7.2506</td>
</tr>
<tr>
<td>42.8243</td>
</tr>
<tr>
<td>502.7281</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>bosonic grid (im): 0.1995E-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3979</td>
</tr>
<tr>
<td>7.2506</td>
</tr>
<tr>
<td>42.8243</td>
</tr>
<tr>
<td>502.7281</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>fermionic grid (im): 0.2003E-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8065</td>
</tr>
<tr>
<td>8.6543</td>
</tr>
<tr>
<td>51.5185</td>
</tr>
<tr>
<td>1022.1852</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>time grid: 0.6315E-12</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0009</td>
</tr>
<tr>
<td>0.0628</td>
</tr>
<tr>
<td>0.4195</td>
</tr>
<tr>
<td>2.5647</td>
</tr>
</tbody>
</table>

NTAUPAR is set automatically based on the available memory: either set manually by means of the MAXMEM-tag, or read from /proc/meminfo (MemAvailable)

“frequency”

“time”
Distributing 16 bosonic points into 8 group(s)
Group: 1 has 1 cores and 2 bosonic point(s)
Group: 2 has 1 cores and 2 bosonic point(s)
Group: 3 has 1 cores and 2 bosonic point(s)
Group: 4 has 1 cores and 2 bosonic point(s)
Group: 5 has 1 cores and 2 bosonic point(s)
Group: 6 has 1 cores and 2 bosonic point(s)
Group: 7 has 1 cores and 2 bosonic point(s)
Group: 8 has 1 cores and 2 bosonic point(s)

Distributing 16 fermionic points into 8 group(s)
Group: 1 has 1 cores and 2 fermionic point(s)
Group: 2 has 1 cores and 2 fermionic point(s)
Group: 3 has 1 cores and 2 fermionic point(s)
Group: 4 has 1 cores and 2 fermionic point(s)
Group: 5 has 1 cores and 2 fermionic point(s)
Group: 6 has 1 cores and 2 fermionic point(s)
Group: 7 has 1 cores and 2 fermionic point(s)
Group: 8 has 1 cores and 2 fermionic point(s)

Distributing 16 time points into 8 group(s)
Group: 1 has 1 cores and 2 time point(s)
Group: 2 has 1 cores and 2 time point(s)
Group: 3 has 1 cores and 2 time point(s)
Group: 4 has 1 cores and 2 time point(s)
Group: 5 has 1 cores and 2 time point(s)
Group: 6 has 1 cores and 2 time point(s)
Group: 7 has 1 cores and 2 time point(s)
Group: 8 has 1 cores and 2 time point(s)

min. memory requirement per mpi rank 448.9 MB, per node 3591.2 MB

Performance-wise it is optimal to have NTAUPAR = NOMEGAPAR = NOMEGA. Prerequisite: there has to be enough memory for NTAUPAR = NOMEGA, and the number of MPI-ranks must be a multiple of NOMEGA.
### OUTCAR: plane wave basis set limit

**ENCUTGW (= 2/3 ENCUT)**  
**ENCUTGWSOFT (= 0.8 ENCUTGW)**

<table>
<thead>
<tr>
<th>cutoff energy</th>
<th>smooth cutoff</th>
<th>RPA correlation</th>
<th>Hartree contr. to MP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>182.607</td>
<td>146.086</td>
<td>-11.6224735165</td>
<td>-18.3767216933</td>
</tr>
<tr>
<td>173.912</td>
<td>139.129</td>
<td>-11.5729431431</td>
<td>-18.3208811769</td>
</tr>
<tr>
<td>165.630</td>
<td>132.504</td>
<td>-11.516771988</td>
<td>-18.2570942952</td>
</tr>
<tr>
<td>157.743</td>
<td>126.194</td>
<td>-11.4562166727</td>
<td>-18.1878044293</td>
</tr>
<tr>
<td>150.232</td>
<td>120.185</td>
<td>-11.3922444110</td>
<td>-18.1141897888</td>
</tr>
<tr>
<td>143.078</td>
<td>114.462</td>
<td>-11.3188094759</td>
<td>-18.0290907645</td>
</tr>
<tr>
<td>136.264</td>
<td>109.012</td>
<td>-11.226196896</td>
<td>-17.9208940815</td>
</tr>
<tr>
<td>129.776</td>
<td>103.821</td>
<td>-11.1299318178</td>
<td>-17.8073101088</td>
</tr>
</tbody>
</table>

**linear regression converged value**  

-12.3629185205  

-19.2342034424

"Extrapolated to infinite basis set limit": \[ E_c(G) = E_c(\infty) + \frac{A}{G^3} \]

### Convergence tests:
- Investigate convergence w.r.t. ENCUT (not ENCUTGW or ENCUTGWSOFT).
- If possible converge energy differences not absolute correlation energies.
OUTCAR: RPA total energy

HF energy using frozen KS orbitals
Free energy of the ion-electron system (eV)

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSCENC</td>
<td>10.57645478</td>
</tr>
<tr>
<td>TEWEN</td>
<td>-285.31033112</td>
</tr>
<tr>
<td>DENC</td>
<td>-32.94127495</td>
</tr>
<tr>
<td>EXHF</td>
<td>74.67798493</td>
</tr>
<tr>
<td>XCENC</td>
<td>0.00000000</td>
</tr>
<tr>
<td>PAW double counting</td>
<td>1473.50548166</td>
</tr>
<tr>
<td>EENTRO</td>
<td>-1473.60386908</td>
</tr>
<tr>
<td>EATOM</td>
<td>229.23716772</td>
</tr>
<tr>
<td>TOTEN</td>
<td>-25.11173175 eV</td>
</tr>
<tr>
<td>ACFDT corr.</td>
<td>-0.00000000</td>
</tr>
<tr>
<td>EDMP2</td>
<td>-19.23420344</td>
</tr>
<tr>
<td>ERPA</td>
<td>-12.36291852</td>
</tr>
<tr>
<td>EGWGM</td>
<td>0.00000000</td>
</tr>
</tbody>
</table>

HF+correlation energy = -36.73420527
HF+E_corr(extrapolated) = -37.47465027

Without extrapolation

“Extrapolated to infinite basis set limit”
RPA: important INCAR tags

- ALGO
- NOMEGA
- PRECFOCK
- NTAUPAR
- NOMEgapar
- MAXMEM
- NBANDS
- NBANDSEXACT
- ENCUTGW

Visit our [WIKI!](#)

Especially the parts on: [Cubic scaling RPA calculations](#)
Cubic-Scaling GW
P. Liu, M. Kaltak, J. Klimeš, and G. Kresse, PRB 94, 165109 (2016)

\[ G_0(i\tau) \xrightarrow{\chi = -GG} \chi_0(i\tau) \xrightarrow{\text{CT}} \chi_0(i\omega) \]

\[ \Sigma(i\tau) \xrightarrow{\Sigma = GW} W(i\tau) \xrightarrow{\text{CT}} W(i\omega) \]

\[ G = \frac{1}{G_0^{-1} - \Sigma} \xrightarrow{\text{analytic continuation}} \Sigma(i\omega) \xrightarrow{\text{Solve QP-equation}} E_{nk}^{\text{QP}} \]

\[ W = \frac{\nu}{1 - \chi \nu} \]
• Minimax grids:
  M. Kaltak, J. Klimeš, and G. Kresse, JCTC 10, 2498 (2014); PRB 90, 054115 (2014).

• Cubic-scaling RPA total energies (ACFDT):
  M. Kaltak, J. Klimeš, and G. Kresse, PRB 90, 054115 (2014).

• Cubic-scaling RPA quasi-particles (GW):

• Finite temperature grids (!):
  M. Kaltak and G. Kresse, PRB 101, 205145 (2020)

Dr. Merzuk Kaltak
(VASP Software GmbH)
Forces in the RPA

\[
\frac{\partial E}{\partial R} = \langle \psi | \frac{\partial H}{\partial R} | \psi \rangle + \langle \frac{\partial \psi}{\partial R} | H | \psi \rangle + \langle \psi | H | \frac{\partial \psi}{\partial R} \rangle
\]

Non-Hellmann-Feynman!

**Hellmann-Feynman theorem:** when the orbitals are eigenstates of the Hamiltonian, the second and third terms on the RHS are zero.

In the RPA we need to consider "non-Hellmann-Feynman" contributions!

These take the following form:

\[
\langle \frac{\partial \psi}{\partial R} | H | \psi \rangle + \langle \psi | H | \frac{\partial \psi}{\partial R} \rangle \rightarrow \left( \int G_0(i\omega) \frac{\partial E_{\text{RPA}}}{\partial G} \bigg|_{i\omega} G_0(i\omega)d\omega \right) \frac{\partial V_{\text{KS}}}{\partial R}
\]

\[
\frac{\partial E_H}{\partial G} = V_H \quad \frac{\partial E_X}{\partial G} = V_X \quad \frac{\partial E_c}{\partial G} = \Sigma
\]

“from linear response”
Forces in the RPA

A test: "RPA forces" (lines) vs. energy derivatives from finite differences (symbols):

(Diamond 8 atom super cell)
Diamond (128 atom super cell)

RPA

PBE

Frequency [cm⁻¹]

Γ X Γ L

RPA

Graphite (128 atom super cell)

PBE

Frequency [cm⁻¹]

A Γ M K Γ
Summary

• Beyond DFT: the RPA
  • Well balanced description of all bond types (metallic, covalent, ionic, vdW)
  • Unfortunately energy differences can still not be predicted with chemical accuracy
  • But at the moment the optimal balance between accuracy and computational effort

• Cubic-Scaling RPA
  • Both for total energies as well as for quasi-particles
  • Minimax frequency and time grids
  • Near future: finite temperature RPA

• Forces in the RPA
The End

Thank you for your attention!