VASP: DFT and Beyond

Martijn Marsman, and Georg Kresse

Computational Materials Physics, Faculty of Physics, University Vienna, Vienna, Austria

Theory and Computation for Interface Science and Catalysis, 3-7th November 2014, Brookhaven National Laboratories, USA
Overview

- **Past**
  - The Workhorse: DFT
  - Efficient and stable algorithms
  - PAW potential database
- **Present**
  - Beyond DFT, and beyond the groundstate:
    - Hybrid functionals, linear response, GW, BSE, ACFDT(RPA)
- **Future**
  - Near future: cubic-scaling-RPA (ACFDT & GW)
  - ...
The Workhorse: Kohn-Sham DFT

\[ \hat{H} \Psi(r_1, ..., r_N) = E \Psi(r_1, ..., r_N) \]

\[ \Psi(r_1, ..., r_N) \quad (#\text{grid points})^N \]

5 electrons on a 10×10×10 grid ~ 10 PetaBytes

\[ \Psi(r_1, ..., r_N) = \prod_{i}^{N} \psi_i(r_i) \quad \rho(r) = \sum_{i}^{N} |\psi_i(r)|^2 \]

\[ E[\rho] = T_s[\{\psi_i[\rho]\}] + E_H[\rho] + E_{xc}[\rho] + E_Z[\rho] + U[Z] \]

\[ \left(-\frac{1}{2} \Delta + V_Z(r) + V_H[\rho](r) + V_{xc}[\rho](r)\right)\psi_i(r) = \epsilon_i \psi_i(r) \]

\[ E_{xc}[\rho] = ??? \quad V_{xc}[\rho](r) = ??? \quad \rightarrow \text{Approximations: LDA, PBE, ...} \]
The Self-Consistency Cycle

\[ H = \langle G | \hat{H} [\rho] | G' \rangle \rightarrow \text{diagonalize } H \rightarrow \{ \psi_i, \epsilon_i \} \quad i = 1, \ldots, N_{\text{FFT}} \]

\[ \rho_0 \rightarrow H_0 \rightarrow \rho' \rightarrow \rho_1 = f(\rho_0, \rho') \rightarrow H_1 \rightarrow \ldots \]

- In practice:
  - Iterative matrix diagonalization
  - blocked-Davidson
  - RMM-DIIS
  - Charge density mixing
  - Broyden mixer
  - Orthonormalization
    - (bottleneck)

  ![Diagram of the self-consistency cycle](image)
Fast, robust, and unchanged since 1995

G. Kresse and J. Furthmüller, PRB 54, 11169 (1996)
Pseudopotentials & the PAW method


- Full potential (“all-electron” method)
- Frozen-core approximation: but core-valence interaction is treated at the same level as valence-valence.
- Pseudo wave function expressed in plane waves
- LCAO correction inside atom-centered spheres

\[ |\psi_n\rangle = |\tilde{\psi}_n\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{\phi}_i | \tilde{\psi}_n \rangle \]

AE \quad = \quad \text{pseudo} \quad \text{pseudo-onsite} \quad \text{AE-onsite}
The PAW method (cont.)

$|\tilde{\psi}_n\rangle$

$|\tilde{\psi}_n\rangle - \sum_i |\phi_i\rangle \langle \tilde{p}_i | \tilde{\psi}_n\rangle$

$|\tilde{\psi}_n\rangle - \sum_i |\phi_i\rangle \langle \tilde{p}_i | \tilde{\psi}_n\rangle + \sum_i |\phi_i\rangle \langle \tilde{p}_i | \tilde{\psi}_n\rangle$

Si scattering properties

Troullier-Martins

PAW
Δ-evaluation (PAW vs. FLAPW)


\[ \Delta = \left( \sqrt{\frac{\int \Delta E^2(V) dV}{\Delta V}} \right) \]

<table>
<thead>
<tr>
<th>E</th>
<th>meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>code 1</td>
<td></td>
</tr>
<tr>
<td>code 2</td>
<td></td>
</tr>
</tbody>
</table>

Δ(PAW)\(_{(\text{VASP})}\) = 0.7 meV/atom

N.B. Δ = 0.7 meV/atom, and not 1.9 meV/atom (as published in Crit. Rev.)
\[ \Delta = \left( \sqrt{ \frac{\int \Delta E^2(V) dV}{\Delta V} } \right) \]

And the very best we can do (with reworked *GW potentials)

\[ \Delta(\text{PAW})_{\text{(VASP)}} = 0.4 \text{ meV/atom} \]
Ultrathin PdO on Pd

- Complex reconstructions:
  - Different from bulk oxide
  - Not a straightforward continuation of the substrate
  - Bulk building blocks rearranged in new ways
Ultrathin PdO layer on Pd(111): STM

Lundgren et al., PRL 88, 246101 (2002)
Core level shifts

Lundgren et al., PRL 88, 246101 (2002)

FIG. 3. HRCL spectra from the O 1s and the Pd 3d\textsubscript{5/2} levels of the surface oxide [21]. Calculated binding energies (averages over groups of atoms with equivalent sites) are indicated as vertical lines.
Aluminium oxide on NiAl(110)

- Non-stoichiometric: not $\text{Al}_2\text{O}_3$ but $\text{Al}_{10}\text{O}_{13}$
  - not $(\text{NiAl})\cdot\text{Al}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$
  - but $(\text{NiAl})\cdot\text{Al}_2\text{O}_3\cdot\text{Al}_3\text{O}_3$ (approximately)
- Remove Al atoms, molecular dynamics at finite temperature

Kresse et al., Science 308, 1440 (2005)
HREELS

High Resolution Electron-Electron Loss Spectroscopy: measures the energy loss of incident electrons when inelastically scattered on matter (vibrational and electronic excitations).


Kresse et al., Science 308, 1440 (2005)
Catalysis: dehydrogenation of propane in Mordenite

\[
\begin{align*}
&MOR-Zn + C_3H_8 \rightarrow MOR-Zn \cdots C_3H_8, \\
&MOR-Zn \cdots C_3H_8 \rightarrow H \cdots MOR-Zn-C_3H_7, \\
&H \cdots MOR-Zn-C_3H_7 \rightarrow MOR-Zn \cdots C_3H_6 + H_2, \\
&MOR-Zn \cdots C_3H_6 \rightarrow MOR-Zn + C_3H_6.
\end{align*}
\]
Beyond DFT?

Lattice constants and Bulk moduli:
AIP, AlAs, BAs, BP, Si, C, SiC, MgO, and LiF

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δa₀</td>
<td>-1.4</td>
<td>3.5</td>
<td>0.8</td>
</tr>
<tr>
<td>ΔB₀</td>
<td>0.8</td>
<td>-7.2</td>
<td>0.4</td>
</tr>
<tr>
<td>MRE</td>
<td>1.4</td>
<td>7.9</td>
<td>0.8</td>
</tr>
<tr>
<td>MARE</td>
<td>0.8</td>
<td>7.2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

(All in %)

Atomization energy

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>PBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MRE (%)</td>
<td>17.3</td>
<td>-1.9</td>
</tr>
<tr>
<td>MARE (%)</td>
<td>17.3</td>
<td>3.4</td>
</tr>
<tr>
<td>ME (eV)</td>
<td>0.76</td>
<td>0.14</td>
</tr>
</tbody>
</table>

(More) accurate treatment of electronic correlation needed for, e.g.:

Band gaps (optical properties)

Total energy differences with chemical accuracy
(1 kcal/mol ≈ 40 meV):
atomization and formation energies
reaction barriers
van der Waals interactions

Band gaps
New Functionals

- New “density” functionals
  - GGA: AM05, PBEsol
  - meta-GGA: TPSS, revTPSS, M06-L
  - VdW-density functionals
- Hybrid functionals
New density functionals (for solids)

AM05

PHYSICAL REVIEW B 72, 085108 (2005)

Functional designed to include surface effects in self-consistent density functional theory

R. Armiento\textsuperscript{1,*} and A. E. Mattsson\textsuperscript{2,†}
\textsuperscript{1}Department of Physics, Royal Institute of Technology, AlbaNova University Center, SE-106 91 Stockholm, Sweden
\textsuperscript{2}Computational Materials and Molecular Biology MS 1110, Sandia National Laboratories, Albuquerque, New Mexico 87185-1110, USA

PBEsol

PRL 100, 136406 (2008)

Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces

John P. Perdew,\textsuperscript{1} Adrienn Ruzsinszky,\textsuperscript{1} Gábor I. Csonka,\textsuperscript{2} Oleg A. Vydrov,\textsuperscript{3} Gustavo E. Scuseria,\textsuperscript{3} Lucian A. Constantin,\textsuperscript{4} Xiaolan Zhou,\textsuperscript{1} and Kieron Burke\textsuperscript{5}
\textsuperscript{1}Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118, USA
\textsuperscript{2}Department of Chemistry, Budapest University of Technology and Economics, H-1521 Budapest, Hungary
\textsuperscript{3}Department of Chemistry, Rice University, Houston, Texas 77005, USA
\textsuperscript{4}Donostia International Physics Center, E-20018, Donostia, Basque Country
\textsuperscript{5}Departments of Chemistry and of Physics, University of California, Irvine, Irvine, California 92697, USA

Better description of lattice constants and bulk moduli, and (jellium) surface energies
TABLE I. Statistical data for the equilibrium lattice constants (Å) of the 18 test solids of Ref. 38 at 0 K calculated from the SJEOS. The Murnaghan EOS yields identical results within the reported number of decimal places. Experimental low temperature (5–50 K) lattice constants are from Ref. 56 (Li), Ref. 57 (Na, K), Ref. 58 (Al, Cu, Rh, Pd, Ag), and Ref. 59 (NaCl). The rest are based on room temperature values from Ref. 60 (C, Si, SiC, Ge, GaAs, NaF, LiF, MgO) and Ref. 57 (LiCl), corrected to the \( T=0 \) limit using the thermal expansion from Ref. 58. An estimate of the zero-point anharmonic expansion has been subtracted out from the experimental values (cf. Table II). (The calculated values are precise to within 0.001 Å for the given basis sets, although GAUSSIAN GTO1 and GTO2 basis-set incompleteness limits the accuracy to 0.02 Å.) GTO1: the basis set used in Ref. 38. GTO2: For C, Si, SiC, Ge, GaAs, and MgO, the basis sets were taken from Ref. 41. For the rest of the solids, the GTO1 basis sets and effective core potentials from Ref. 38 were used. The best theoretical values are in boldface. The LDA, PBEsol, and PBE GTO2 results are from Ref. 14. The SOGGA GTO1 results are from Ref. 15.

<table>
<thead>
<tr>
<th></th>
<th>LDA GTO2</th>
<th>LDA VASP</th>
<th>PBEsol GTO2</th>
<th>PBEsol BAND</th>
<th>PBEsol VASP</th>
<th>AM05 VASP</th>
<th>SOGGA GTO1</th>
<th>PBE VASP</th>
<th>PBE BAND</th>
<th>PBE TPSS</th>
<th>PBE VASP</th>
<th>PBE BAND</th>
<th>PBE TPSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME(^a) (Å)</td>
<td>-0.047</td>
<td>-0.055</td>
<td>0.022</td>
<td><strong>0.010</strong></td>
<td><strong>0.012</strong></td>
<td>0.029</td>
<td><strong>0.009</strong></td>
<td>0.075</td>
<td>0.066</td>
<td>0.063</td>
<td>0.048</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAE(^b) (Å)</td>
<td>0.050</td>
<td>0.050</td>
<td>0.030</td>
<td><strong>0.023</strong></td>
<td><strong>0.023</strong></td>
<td>0.036</td>
<td><strong>0.024</strong></td>
<td>0.076</td>
<td>0.069</td>
<td>0.067</td>
<td>0.052</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MRE(^c) (%)</td>
<td>-1.07</td>
<td>-1.29</td>
<td>0.45</td>
<td><strong>0.19</strong></td>
<td><strong>0.24</strong></td>
<td>0.58</td>
<td><strong>0.19</strong></td>
<td>1.62</td>
<td>1.42</td>
<td>1.35</td>
<td>0.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MARE(^d) (%)</td>
<td>1.10</td>
<td>1.15</td>
<td>0.67</td>
<td><strong>0.52</strong></td>
<td><strong>0.52</strong></td>
<td>0.80</td>
<td><strong>0.50</strong></td>
<td>1.65</td>
<td>1.48</td>
<td>1.45</td>
<td>1.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Meta-GGAs

<table>
<thead>
<tr>
<th>Lattice constant</th>
<th>MRE</th>
<th>MARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>-1.73</td>
<td>1.73</td>
</tr>
<tr>
<td>PBE</td>
<td>1.10</td>
<td>1.29</td>
</tr>
<tr>
<td>PBEsol</td>
<td>-0.24</td>
<td>0.73</td>
</tr>
<tr>
<td>AM05</td>
<td>0.19</td>
<td>0.75</td>
</tr>
<tr>
<td>TPSS</td>
<td>0.73</td>
<td>0.90</td>
</tr>
<tr>
<td>rev TPSS</td>
<td>0.29</td>
<td>0.68</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomization energy (solids)</th>
<th>MRE</th>
<th>MARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>16.5</td>
<td>16.5</td>
</tr>
<tr>
<td>PBE</td>
<td>-3.68</td>
<td>4.23</td>
</tr>
<tr>
<td>PBEsol</td>
<td>5.97</td>
<td>6.52</td>
</tr>
<tr>
<td>TPSS</td>
<td>-1.99</td>
<td>4.70</td>
</tr>
<tr>
<td>rev TPSS</td>
<td>1.22</td>
<td>5.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomization energy (AE6 mol.)</th>
<th>MRE</th>
<th>MARE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE</td>
<td>3.2</td>
<td>4.2</td>
</tr>
<tr>
<td>PBEsol</td>
<td>8.1</td>
<td>8.1</td>
</tr>
<tr>
<td>TPSS</td>
<td>1.3</td>
<td>2.4</td>
</tr>
<tr>
<td>rev TPSS</td>
<td>1.3</td>
<td>2.8</td>
</tr>
</tbody>
</table>

(All in %)

\[
E_{xc} = \int dr \rho(r) \epsilon_{xc}[\rho(r), \nabla \rho(r), \tau(r)]
\]

\[
\tau(r) = \sum_i 1/2 |\nabla \psi_i(r)|^2
\]

FIG. 1. (Color) (a) Atop CO desorption energy vs surface energies for Pt(111) and Rh(111). RPA values from Ref. 5, experimental surface energies from liquid-metal data (Refs. 23 and 24), and experimental CO desorption energies from Ref. 7. Surface energies are per surface-plane atom. (b) Exchange enhancement factors of

$$E_{c}^{nl} = \int \int \rho(r) \phi(r, r') \rho(r') dr dr'$$

Van der Waals - DFT

![Graph showing binding energy differences for different geometries: Prism, Cage, Book, Cyclic, with various functionals: Reference, revPBE-vdW, optB88-vdW, BLYP-vdW(Silv.), PBE-vdW(TS), PBE.](image)
Hybrid functionals

Hartree-Fock-DFT hybrid:

\[ E_{xc}^{hyb.} = aE_X^{HF} + (1 - a)E_X^{DFT} + E_c^{DFT} \]

where

\[ E_x^{HF} \propto \sum_{kn,qm} \int \int d^3rd^3r' \frac{\psi_{kn}^*(r)\psi_{qm}(r)\psi_{qm}^*(r')\psi_{kn}(r')}{|r - r'|} \]

Solve a one-electron equation:

\[ \left( -\frac{1}{2}\Delta + V_Z(r) + V_H[n](r) \right)\psi_i(r) + \int V_X(r, r')\psi_i(r')dr' = \epsilon_i\psi_i(r) \]

with an orbital dependent, non-local potential \( V_X(r, r') \) (compare to DFT)
How do they perform?

Figure 8. Band gaps from PBE, PBE0, and HSE03 calculations, plotted against data from experiment.
Defects in ZnO

What is the source of n-type conductivity in ZnO?

- Oxygen vacancy:
  - low formation energy
  - deep trap
- Zink interstitial:
  - shallow donor
  - high formation energy
- So?
  - Possibly: Hydrogen
  - Still not solved ...

OBA et al. PHYSICAL REVIEW B 77, 245202 (2008)
One-electron picture

DFT

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

HF-DFT Hybrids

\[
\left( -\frac{1}{2} \Delta + V_{\text{ext}}(r) + V_{\text{H}}(r) \right) \psi_{n_k}(r) + \int V_X(r, r') \psi_{n_k}(r') dr' = \epsilon_{n_k} \psi_{n_k}(r)
\]

GW quasiparticles

\[
\left( -\frac{1}{2} \Delta + V_{\text{ext}}(r) + V_{\text{H}}(r) \right) \psi_{n_k}(r) + \int \Sigma(r, r', E_{n_k}) \psi_{n_k}(r') dr' = E_{n_k} \psi_{n_k}(r)
\]
\[
\left( -\frac{1}{2} \Delta + V_{\text{ext}}(r) + V_{\text{H}}(r) \right) \psi_{nk}(r) + \int \Sigma(r, r', E_{nk}) \psi_{nk}(r') dr' = E_{nk} \psi_{nk}(r)
\]

The “self-energy”:
\[
\Sigma = iGW
\]

The Green's function:
\[
G(r, r', \omega) = \sum_n \frac{\psi_n(r) \psi_n^*(r')}{\omega - \epsilon_n + i\eta \text{sgn}(\epsilon_n - \mu)}
\]

Screened Coulomb int. \quad \text{dielectric screening} \quad \text{Random-Phase-Approx. (RPA)}
\[
W = \epsilon^{-1} \nu \\
\epsilon^{-1} = 1 + \nu \chi \\
\chi = \chi^0 + \chi^0 \nu \chi
\]

IP polarizability (Adler&Wiser), the bottleneck (scales as $N^4$):
\[
\chi^0_{G, G'}(q, \omega) = \frac{1}{\Omega} \sum_{nn'k} 2w_k (f_{n'k+q} - f_{nk})
\]
\[
\times \frac{\langle \psi_{n'k+q} | e^{i(q+G)r} | \psi_{nk} \rangle \langle \psi_{nk} | e^{-i(q+G')r'} | \psi_{n'k+q} \rangle}{\epsilon_{n'k+q} - \epsilon_{nk} - \omega - i\eta}
\]
G0W0(PBE) and GW0 QP-gaps

\[ G_0W_0: \text{MARE}=8.5\% \quad \text{and} \quad GW_0: \text{MARE}=4.5\% \]
Fully self-consistent GW
G. Kresse et al., PRL 99, 246403 (2007)
Bethe-Salpeter-Equation
\[ \Delta(\text{PAW})_{\text{VASP}} = 0.4 \text{ meV/atom} \]
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

\[
E_c = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}\left\{\ln[1 - \chi^0(i\omega)\nu] + \chi^0(i\omega)\nu\right\}
\]

The main effort is again computing the IP-polarizability:

\[
\chi_{GG'}^0(q, i\omega) = \frac{1}{V} \sum_{n,n',k} 2g_k(f_{n'k+q} - f_{nk}) \times \frac{\langle \psi_{n'k+q} | e^{i(q+G)r} | \psi_{nk} \rangle \langle \psi_{nk} | e^{-i(q+G')r} | \psi_{n'k+q} \rangle}{\epsilon_{n'k+q} - \epsilon_{nk} - i\omega}
\]
RPA: lattice constants
J. Harl et al., PRB 81, 115126 (2010)
RPA: heats of formation

TABLE I. Heats of formation at $T = 0 \text{ K}$ in kJ/mol (per formula unit) with respect to the elemental phases in their normal state under ambient conditions. Experimental values are collected in Ref. [33], if not otherwise stated, and have been corrected for zero-point vibrations (ZPV) (experimental values without corrections are in parentheses). The ZPV have been evaluated using harmonic \textit{ab initio} phonon calculations.

<table>
<thead>
<tr>
<th>Solid</th>
<th>PBE</th>
<th>LDA</th>
<th>EXX</th>
<th>RPA</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF$^a$</td>
<td>570</td>
<td>613</td>
<td>664</td>
<td>609</td>
<td>619 (614)</td>
</tr>
<tr>
<td>NaF</td>
<td>522</td>
<td>558</td>
<td>607</td>
<td>567</td>
<td>577 (573)</td>
</tr>
<tr>
<td>NaCl</td>
<td>355</td>
<td>381</td>
<td>433</td>
<td>405</td>
<td>413 (411)</td>
</tr>
<tr>
<td>MgO$^a$</td>
<td>516</td>
<td>595</td>
<td>587</td>
<td>577</td>
<td>604 (597)</td>
</tr>
<tr>
<td>MgH$_2$ $^a$</td>
<td>52</td>
<td>89</td>
<td>113</td>
<td>72</td>
<td>78 (68)</td>
</tr>
<tr>
<td>AlN</td>
<td>262</td>
<td>327</td>
<td>350</td>
<td>291</td>
<td>321 (313$^b$)</td>
</tr>
<tr>
<td>SiC</td>
<td>51</td>
<td>54</td>
<td>69</td>
<td>64</td>
<td>69 (72)</td>
</tr>
</tbody>
</table>

$^a$bcc Li, hcp Mg, and rutile MgH$_2$ were considered in their experimental geometries, whereas for the other materials the theoretical minimum energy geometries were used.

$^b$Ref. [34].

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

$C_6$ coefficients for noble gas solids

<table>
<thead>
<tr>
<th></th>
<th>RPA(LDA)</th>
<th>RPA(PBE)</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>62</td>
<td>53</td>
<td>47</td>
</tr>
<tr>
<td>Ar</td>
<td>512</td>
<td>484</td>
<td>455</td>
</tr>
<tr>
<td>Kr</td>
<td>1030</td>
<td>980</td>
<td>895</td>
</tr>
</tbody>
</table>
RPA: CO @ Pt(111) and Rh(111)

Too small surface energies and too large adsorption energies!

FIG. 1: Atop CO adsorption and surface energies for Pt(111) and Rh(111). (a) Considered CO adsorption geometries for a (2 x 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, PBEsol, PBE, rPBE, and BLYP, in order of increasing gradient corrections. Furthermore, the hybrid functional HSE based on the PBE functional was used.

FIG. 3: Surface energies, lattice constants and adsorption energies. (a) Surface energies ($E_s$) for PBEsol, BLYP and RPA. Experimental data are from Ref. 24. (b) Lattice constants for PBEsol, RPA and BLYP. (c) Adsorption energies for the atop and hollow sites on Cu, late 4d metals and Pt for PBEsol and RPA and BLYP. Experimental data with error bars are from Ref. 25.

RPA:
Right site preference
Good adsorption energies
Excellent lattice constants
Good surface energies

Evaluate the Green's function in “imaginary” time:

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

and the polarizability as:

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

Followed by a cosine-transform:

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

Now the worst scaling step is

\[ E_c = \int_0^\infty \frac{d\omega}{2\pi} \text{Tr}\{\ln[1 - \chi^0(i\omega)\nu] + \chi^0(i\omega)\nu}\]  

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

But storing \( G \) and \( \chi \) is expensive! \( \rightarrow \) we need small sets of cleverly chosen “\( \tau \)” and “\( \omega \)” 
[see Kaltak et al., JCTC 10, 2498 (2014)]
Cubic scaling in the #atoms

TABLE I. Timings in minutes for an RPA calculation for different bulk Si bcc cells. The calculations are done for the Γ point only and the number of cores is increased with system size. Since one of the computational steps scales only quadratically with system size, the total scaling is better than cubic.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Cores</th>
<th>Time</th>
<th>Time×cores/atoms$^3 \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>32</td>
<td>14.3</td>
<td>2.91</td>
</tr>
<tr>
<td>128</td>
<td>64</td>
<td>83.2</td>
<td>2.54</td>
</tr>
<tr>
<td>250</td>
<td>128</td>
<td>299.9</td>
<td>2.45</td>
</tr>
</tbody>
</table>

PHYSICAL REVIEW B 90, 054115 (2014)
Linear scaling in #k-points

![Graph showing linear scaling with respect to the number of k-points](image)

- **Wall clock time (minutes)**
- **Number of k-points**
  - 64 atoms
  - 128 atoms
  - 216 atoms

*PHYSICAL REVIEW B 90, 054115 (2014)*
Formation energies of defects in Si

<table>
<thead>
<tr>
<th></th>
<th>216 atom</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\Gamma$</td>
<td>2</td>
<td>4</td>
<td>PBE</td>
<td>RPA</td>
</tr>
<tr>
<td>X(PBE)</td>
<td></td>
<td>3.256</td>
<td>3.341</td>
<td>3.571</td>
<td>3.566</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td></td>
<td>0.724</td>
<td>0.710</td>
<td>0.632</td>
<td>3.566</td>
<td>4.20</td>
</tr>
<tr>
<td>C$_3$</td>
<td></td>
<td>0.820</td>
<td>0.812</td>
<td>0.743</td>
<td>3.619</td>
<td>4.36</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td>0.789</td>
<td>0.779</td>
<td>0.707</td>
<td>3.626</td>
<td>4.33</td>
</tr>
<tr>
<td>T</td>
<td></td>
<td>1.105</td>
<td>1.144</td>
<td>1.139</td>
<td>3.791</td>
<td>4.93</td>
</tr>
<tr>
<td>VJT</td>
<td></td>
<td>0.789</td>
<td>0.755</td>
<td>0.742</td>
<td>3.646</td>
<td>4.39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>256 atom</th>
<th></th>
<th></th>
<th>PBE</th>
<th>RPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>VJT(PBE)</td>
<td></td>
<td>3.272</td>
<td>3.518</td>
<td>3.589</td>
<td></td>
</tr>
<tr>
<td>VJT</td>
<td></td>
<td>0.839</td>
<td>0.745</td>
<td>3.589</td>
<td>4.33</td>
</tr>
</tbody>
</table>
The End

Thank you!