ASSESSMENT OF DFT METHODS FOR SOLIDS

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DFT: a quick overview

The Jacob’s Ladder

DFT energy
Hohenberg, Kohn; Phys. Rev. 1964, 136, 864
Kohn, Sham, Phys. Rev. 1965, 140, 1133

E=E[\rho(r)]=E_{\text{nuclear}} + E_{\text{kinetic}} + E_{\text{nucl-electron}} + E_{\text{coulomb}} + E_{\text{XC}}

DFT HEAVEN

Exact exchange, exact partial correlation
Exact exchange, compatible correlation
meta-GGA
GGA
LDA
HARTREE WORLD

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DFT: a quick overview

PBE’s type exchange functionals

\[ E_X = \sum_\sigma \int \rho_\sigma \varepsilon_{X,\sigma}[\rho_\sigma] F(s_\sigma[\rho_\sigma, \nabla \rho_\sigma]) \, dr \]

Spin density

Reduced spin density

Exchange energy density

Different forms of \( F(s_\sigma) \) were proposed:

- PBE (1996)
- revPBE (1998)
- RPBE (1999)
- mPBE (2002)
- WC* (2006)
- PBEsol* (2008)
- SOGGA* (2008) \([1/2 \text{ PBE} + 1/2 \text{ RPBE}]\)

*CRYSTAL09 (B. Civalleri - 2008)
DFT: a quick overview

HF/DFT hybrid functionals

\[ E_{XC} = a \cdot [E_X(HF) - E_X(DFT)] + E_{XC}(DFT) \]
(e.g. PBE0)

\[ E_X = (1-a) \cdot [E_X(LDA) + b \cdot E_X(XXX)] + a \cdot E_X(HF) \]
\[ E_C = (1-c) \cdot E_C(VWN) + c \cdot E_C(YYY) \]
(XXX, YYY: non-local exchange and correlation)
(e.g. B3LYP: XXX=B, YYY=LYP
B3PW: XXX=B, YYY=PW91)

\[ a = \text{fraction of exact exchange} \]
Use of hybrid functionals in solid state simulation

*a matter of discussion* in the scientific community
- claimed lacks in accuracy
- use of empirical parameters
- bad description of narrow-gap and conducting systems
- ...

*largely diffuse* (e.g. B3LYP, B3PW, PBE0) and often proved to provide the best results for structural, electronic, thermodynamical and dynamical properties of non-conducting systems (in particular H-containing systems)


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DFT: a quick overview

HF/DFT hybrid functionals
The example of Brucite, Mg(OH)$_2$

Differences between calculated and experimental results:
- a,c: lattice parameters, Å
- $\Delta V\%$: volumes, relative difference (calc-exp)/exp*100
- OH: bond length of OH group, Å
- v: anharmonic stretching of the OH oscillator, cm$^{-1}$
## DFT: a quick overview

### HF/DFT hybrid functionals

<table>
<thead>
<tr>
<th>J/K</th>
<th>pyrope</th>
<th>grossular</th>
<th>andradite</th>
<th>spessartine</th>
<th>uvarovite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SVWN</td>
<td>SVWN</td>
<td>PBE</td>
<td>PBE</td>
<td>B3LYP</td>
<td>PBE0</td>
</tr>
<tr>
<td>KMnF&lt;sub&gt;3&lt;/sub&gt; exchange coupling constant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Calculated vs experimental dielectric constants of garnets. No experimental data for almandine

A. Meyer, M. Ferrero, L. Valenzano, C. M. Zicovich-Wilson, R. Orlando, R. Dovesi
In preparation
DFT & CRYSTAL

CRYSTAL input for DFT calculation

title
1 - GEOMETRY block
2 - BASIS SET block
3 - HAMILTONIAN and SCF block

Structure of CRYSTAL input

Options:
1 - Choice of the exchange-correlation functionals
2 - Integration grid and numerical accuracy control
3 - Atomic parameters
(and add SPIN for open-shell systems)

In block 3:

DFT

options

END

DFT input block

For points 2-3 default values are supplied
Point 1 must be set
## DFT & CRYSTAL

### DFT functionals available in CRYSTAL

<table>
<thead>
<tr>
<th>EXCHANGE</th>
<th>CORRELATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>PWLSD</td>
</tr>
<tr>
<td></td>
<td>VWN</td>
</tr>
<tr>
<td></td>
<td>PZ</td>
</tr>
<tr>
<td></td>
<td>VBH</td>
</tr>
<tr>
<td>LDA (=S)</td>
<td></td>
</tr>
<tr>
<td>VBH</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GGA</th>
<th>BECKE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PWGGA (=PW91)</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
</tr>
<tr>
<td></td>
<td>PBESOL*</td>
</tr>
<tr>
<td></td>
<td>WCGGA* (=WC)</td>
</tr>
<tr>
<td></td>
<td>SOGGA*</td>
</tr>
<tr>
<td>BECKE</td>
<td>LYP</td>
</tr>
<tr>
<td>PWGGA (=PW91)</td>
<td>PBE</td>
</tr>
<tr>
<td>PBE</td>
<td>PBESOL*</td>
</tr>
<tr>
<td>PBESOL*</td>
<td></td>
</tr>
<tr>
<td>WCGGA*</td>
<td></td>
</tr>
<tr>
<td>SOGGA*</td>
<td></td>
</tr>
<tr>
<td>*CRYSTAL09</td>
<td>(References in the CRYSTAL users’ manual)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1 - Choice of the functional

- DFT
- EXCHANGE
- CORRELAT
- HYBRID
- NONLOCAL

- If not set, \( E_X(HF) \) used
- If not set, no \( E_C \)
- Percentage of \( E_X(HF) \), if not set: pure DFT
- Non-local weighting parameters for \( E_C \)
1 - Choice of the functional

<table>
<thead>
<tr>
<th>GLOBAL KEYWORDS</th>
<th>EXCHANGE</th>
<th>CORRELAT</th>
<th>HYBRID</th>
<th>NONLOCAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOGGAXC*</td>
<td>SOGGA</td>
<td>PBE</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PBE1PBE* (PBE0)</td>
<td>PBE</td>
<td>PBE</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>B3PW</td>
<td>BECKE</td>
<td>PWGGA</td>
<td>20</td>
<td>0.9 0.81</td>
</tr>
<tr>
<td>B3LYP</td>
<td>BECKE</td>
<td>LYP</td>
<td>20</td>
<td>0.9 0.81</td>
</tr>
</tbody>
</table>

*CRYSTAL09

(References in the CRYSTAL users’ manual)
$E_{XC}$ and its gradient are evaluated by numerical integration over the cell volume: an integration grid is required

- Grid based on atomic partition method (Becke), $V_{\text{cell}}$ partitioned into atomic volumes: $V_A$ centered on atom A

- Radial and angular components (Gauss-Legendre radial quadrature, Lebedev 2-dimensional angular point distribution; points associated to a weight, $w$)

  Uniform (or unpruned) grid
For reducing the grid size and maintaining its effectiveness:

pruned grid (not radially uniform):

the number of angular points is maximum in the valence region and gradually decreases in both directions
The example of MgO
(R. Orlando - 2006)

- Grid of Mg
- Grid of O

Radial points:
Gauss’ formula
($n_r=$number of radial points)

Angular points:
Lebedev distribution
($L=$Lebedev accuracy parameter)
Integration grid and numerical accuracy control

\[ n_r=55 \ L=13 \quad -275.43121602 \ (31878) \quad -275.43123079 \ (11552) \]
\[ n_r=75 \ L=13 \quad -275.43123518 \ (42956) \quad -275.43123451 \ (20542) \]
\[ n_r=75 \ L=16 \quad -275.43127155 \ (96038) \quad -275.43127167 \ (41530) \]

(R. Orlando - 2006)
Integration grid and numerical accuracy control: use of symmetry

<table>
<thead>
<tr>
<th>Size of Grid</th>
<th>$t_{\text{elapsed}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55, 13</td>
<td>4.41</td>
</tr>
<tr>
<td>75, 13</td>
<td>7.27</td>
</tr>
<tr>
<td>75, 16</td>
<td>14.13</td>
</tr>
</tbody>
</table>

- 11552 513 4.41
- 20542 882 7.27
- 41530 1437 14.13

(R. Orlando - 2006)
2 - Integration grid and numerical accuracy control

RADIAL
... ... ...
ANGULAR
... ... ...

Number of intervals, integration interval limits, number of radial points in the $i^{th}$ interval, $n_r$

Number of intervals, integration interval limits, accuracy level (L) of each integral
### CRYSTAL input for DFT calculation

**2 - Integration grid and numerical accuracy control**

Default grid: \((55,434)p\) -- 434 angular points in the valence region

| RADIAL | 1  
|        | 4.0  
|        | 55  
| ANGULAR | 10  
|        | 0.4 0.6 0.8 0.9 1.1 2.3 2.4 2.6 2.8 9999.0  
|        | 1 2 5 8 11 13 11 8 5 1  
|        | (38 50 110 194 302 434 302 194 110 38)  

Angular points generated

\(n_r\)

\(L\)
2 - Integration grid and numerical accuracy control

GLOBAL KEYWORDS:

<table>
<thead>
<tr>
<th>Grid</th>
<th>NID</th>
<th>Δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEFAULT</td>
<td>119.998710</td>
<td>1.3E-03</td>
</tr>
<tr>
<td>XLGRID</td>
<td>120.000054</td>
<td>-5.4E-05</td>
</tr>
<tr>
<td>XXLGRID</td>
<td>119.999986</td>
<td>1.4E-05</td>
</tr>
<tr>
<td>(n_r=99,L=22)</td>
<td>119.9999999</td>
<td>1.0E-06</td>
</tr>
</tbody>
</table>

Numerically integrated density (NID)
Diaspore, 4AlOOH in the unit cell, 120 electrons

(see CRYSTAL users’ manual for details)
2 - Integration grid and numerical accuracy control

Calcite:

effect of the grid on geometry and vibrational modes

<table>
<thead>
<tr>
<th></th>
<th>default</th>
<th>LGRID</th>
<th>XLGRID</th>
<th>75,16 unpr</th>
<th>75,18 unpr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(55, 434)p</td>
<td>(75, 434)p</td>
<td>(75, 974)p</td>
<td>(75, 974)</td>
<td>(99, 1454)</td>
</tr>
</tbody>
</table>

|       | \(|\Delta|\) | 5.9 | 0.3 | 0.3 | 0 | Reference |
|-------|---------|-----|-----|-----|---|-----------|
|       | \(\Delta_{\text{max}}\) | 47.5 | 19.1 | 0.4 | 0.2 | 0 |
|       | \(\Delta_{\text{min}}\) | -4.1 | -1.3 | -0.9 | -0.9 | 0 |
|       | \(N_p\) | 60 954 | 120 198 | 246 264 | 515 912 | 1 010 024 |
|       | \(\Delta_e\) | 990 | 300 | 20 | 20 | 40 |
|       | \(\Delta E\) | -1436 | -104 | -24 | -26 | 0 |
|       | \(d_{\text{C–O}}\) | 1.2948 | 1.2950 | 1.2947 | 1.2947 | 1.2947 |
|       | \(d_{\text{Ca–O}}\) | 2.3928 | 2.3927 | 2.3929 | 2.3929 | 2.3929 |

18 (IR+Raman+silent)

Average of Abs diff.

Maximum difference

Minimum difference

Grid points

\(\mu\)-electron (TOT: 100 \(e\))

\(\mu\)-hartree

Å

Å

2 - Integration grid and numerical accuracy control

OH vibrational data of brucite: Effect of pruned and unpruned grid size

<table>
<thead>
<tr>
<th>n_r,L</th>
<th>N. points</th>
<th>O-H</th>
<th>v(OH)h</th>
<th>Pruned</th>
<th>Np</th>
<th>O-H</th>
<th>v(OH)h</th>
</tr>
</thead>
<tbody>
<tr>
<td>55,434</td>
<td>77’870</td>
<td>0.9621</td>
<td>3822</td>
<td></td>
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<tr>
<td>75,434</td>
<td>106’210</td>
<td>0.9623</td>
<td>3843</td>
<td>(LGRID)</td>
<td></td>
<td></td>
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<tr>
<td>99,434</td>
<td>140’038</td>
<td>0.9622</td>
<td>3842</td>
<td></td>
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<td></td>
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<tr>
<td>55,974</td>
<td>174’066</td>
<td>0.9619</td>
<td>3824</td>
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<tr>
<td>75,974</td>
<td>237’164</td>
<td>0.9619</td>
<td>3846</td>
<td>(XLGRID)</td>
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<tr>
<td>99,974</td>
<td>311’570</td>
<td>0.9619</td>
<td>3844</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>99,1454</td>
<td>463’462</td>
<td>0.9619</td>
<td>3844</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Pruned)

2 - Integration grid and numerical accuracy control

Details on the grid size and its performance:


2 - Integration grid and numerical accuracy control
- unpruned grid can be set
- thresholds on grid weights and electronic density can be increased or decreased with respect to default
- different methods for the point weights
- keywords for memory management

3 - Atomic parameters - set atomic radius and formal charge different from the computed one

(see CRYSTAL users’ manual for details)
Performance of DFT functionals for describing periodic systems

TEST SYSTEMS: quasi-1D
+ SW-carbon nanotubes
+ SW-chrysotile
+ aluminium hydroxides
+ brucite
+ orthosilicates
+ garnets
3D
+ olivine
+ Si and Al oxides
(+ diamond, silicon
(+ MgO
semi-ionic, H-containing, HBs, layered and non-layered
semi-ionic, H-containing, no HBs, layered
semi-ionic, H-free
“ “
“ “
“ “
pure-covalent, (“) work in progress
pure-ionic, (”) work in progress

TEST FUNCTIONALS: SWVN, SPWLSD (LDA)
PBE, PW91, PBEsol, WC-PBE, SOGGA-PBE (GGA)
B1WC, WC1LYP, B3PW, B3LYP, PBE0 (hybrids)

POSTER N. 4
R. Demichelis, B. Civalleri, Y. Noel and R. Dovesi

MSSC2009 - September, 10th 2009 - Raffaella Demichelis - Assessment of DFT methods for solids
SWCNTs: all the tested DFT functionals (LDA, GGA, hybrids) provide reasonable results for structure, energetics and vibrational frequencies. The choice of Hamiltonian is crucial for the description of the band gap.


Chrysotile: comparison PBE0 vs B3LYP. Both provide good structures and relative stability. PBE0 structural data are however more accurate.

Performance of DFT functionals for describing periodic systems

Aluminosilicates
Performance of DFT functionals for describing periodic systems

ΔV%


Performance of DFT functionals for describing periodic systems

The relative stability of the polymorphs
Performance of DFT functionals for describing periodic systems

The relative stability of the polymorphs

In general:

+ 

+ 

+ 


+ 