Volker Blum

Duke University
Department of Mechanical Engineering and Materials Science
Durham, NC, USA

http://aims.pratt.duke.edu

\[ \hat{H}\Psi = E\Psi \]

https://aimsclub.fhi-berlin.mpg.de
https://elsi-interchange.org

Hands-On Workshop Density Functional Theory and Beyond - HU Berlin, July 31, 2017
Many Individuals Contributed to This Work - Thanks!

Fritz Haber Institute, Berlin

[Richard-Willstätter-Haus]
Many Individuals Contributed to This Work - Thanks!

Dr. William Huhn
Spin-Orbit Coupling
“Energy Materials”

Victor Yu
Electronic Structure Infrastructure (NSF)

Dr. Björn Lange
Jan Kloppenburg
Tiago Botari

FHI-aims team and collaborators: Matthias Scheffler (Berlin), Xinguo Ren (Hefei), Karsten Reuter (Munich), over 100 individuals with contributions to the project. Development in Berlin, Hefei, Munich, Helsinki, London, Duke, Argonne, etc.

Ab Initio Materials Simulations Group
Hudson Hall, Duke University

Dr. Wenhui Mi
(since August 2016)

Dr. Raul Laasner
Nuclear Spin States & NMR

Tong Zhu
PV Materials
GW & RPA

Garnett Liu
Perovskites
Excitonic Effects
Scope of this Lecture

Technical concepts (I):

• Basis sets
• Integrals and grids; electrostatics; molecules vs. periodic solids
• How to deal with relativity
• Scalability (large systems, large computers)

Our implementation: FHI-aims

All-electron, molecules and periodic systems

Main example for this talk (others in the next 10 days)
Used for tutorials in the next 10 days

Kohn-Sham Equations, 1965

\[-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})\]
Some of the Science Pursued in Our Group
Some of the Science Pursued in Our Group

Theory of Contact-Resonance AFM

Images: Oxygen-intercalated graphene on SiC.
wl Zauscher group (Duke); ACS Nano (2016).
Some of the Science Pursued in Our Group

Theory of Contact-Resonance AFM

Images: Oxygen-intercalated graphene on SiC. w/ Zauscher group (Duke); ACS Nano (2016).
Some of the Science Pursued in Our Group

Theory of Contact-Resonance AFM

Images: Oxygen-intercalated graphene on SiC. w/ Zauscher group (Duke); ACS Nano (2016).

Topography

CR-AFM

Model $\rightarrow$ DFT $\rightarrow$ Elastic Model $\rightarrow$ CR-AFM

$C_{33,1}$

$C_{33,2}$

$C_{33,3}$

$C_{33,4}$

$C_{33,5}$

$C_{33,6}$
Some of the Science Pursued in Our Group

Theory of Contact-Resonance AFM

Images: Oxygen-intercalated graphene on SiC. w/ Zauscher group (Duke); ACS Nano (2016).
Some of the Science Pursued in Our Group

**Theory of Contact-Resonance AFM**

Images: Oxygen-intercalated graphene on SiC. w/ Zauscher group (Duke); ACS Nano (2016).

**Beyond-Zincblende Absorbers for PV, PEC**

Cu$_2$BaSn(S$_1$Se$_3$) w/ Mitzi group (Duke); Adv. Mater. (2017): 5% PV prototype efficiency
Some of the Science Pursued in Our Group

Theory of Contact-Resonance AFM

Topography

Images: Oxygen-intercalated graphene on SiC.

w/ Zauscher group (Duke); ACS Nano (2016).

Beyond-Zincblende Absorbers for PV, PEC

Cu$_2$BaSn(Si$_3$Se$_3$)

w/ Mitzi group (Duke);

Understanding C-N H-Evolution Materials

w/ Lotsch group (Stuttgart); Nature Commun. (2016).
Some of the Science Pursued in Our Group

**Theory of Contact-Resonance AFM**

Images: Oxygen-intercalated graphene on SiC. w/ Zauscher group (Duke); ACS Nano (2016).

**Beyond-Zincblende Absorbers for PV, PEC**

Cu$_2$BaSn(S$_1$Se$_3$) w/ Mitzi group (Duke); Adv. Mater. (2017): 5% PV prototype efficiency

**Understanding C-N H-Evolution Materials**

w/ Lotsch group (Stuttgart); Nature Commun. (2016).

**Nuclear Hyperpolarization**

w/ Theis, Warren (Duke); Science Advances (2016).
Some of the Science Pursued in Our Group

**Theory of Contact-Resonance AFM**
- Images: Oxygen-intercalated graphene on SiC.
- w/ Zauscher group (Duke); ACS Nano (2016).

**Beyond-Zincblende Absorbers for PV, PEC**
- Cu$_2$BaSn(S$_1$Se$_3$)
- w/ Mitzi group (Duke);

**Understanding C-N H-Evolution Materials**
- w/ Lotsch group (Stuttgart); Nature Commun. (2016).

**Nuclear Hyperpolarization**
- w/ Theis, Warren (Duke); Science Advances (2016).
Some of the Science Pursued in Our Group

Theory of Contact-Resonance AFM Imaging: Oxygen-intercalated graphene on SiC.

Beyond-Zincblende Absorbers for PV, PEC: Cu$_2$BaSn(S$_3$)

Understanding C-N H-Evolution Materials:

In all these areas, predictive quantum mechanics based simulations can help provide solutions.

Yet, so much more is possible if we can extend their reach! How to make this happen?
Dirac 1929:
“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known ...”
We Have a Predictive Theory for (Almost) Everything!

\[ \hat{H} \Psi = E \Psi \]

Dirac 1929:
“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known …”

\[
\hat{\mathcal{H}} = \sum_{I} \frac{P_{I}^2}{2M_{I}} + \sum_{k} \frac{p_{k}^2}{2m_{e}} + \sum_{I \neq J} \frac{Z_{I}Z_{J}}{2|R_{I} - R_{J}|} + \sum_{I,k} \frac{Z_{I}}{2|R_{I} - r_{k}|} - \sum_{k \neq k'} \frac{1}{2|r_{k} - r'_{k}|}
\]

\[
\Psi \equiv \Psi(\{R_{I}\}, \{r_{k}\})
\]
We Have a Predictive Theory for (Almost) Everything!

\[ \hat{H} \Psi = E \Psi \]

Dirac 1929:
“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known …”

\[
\hat{H} \equiv \sum_I \frac{P_I^2}{2M_I} + \sum_k \frac{p_k^2}{2m_e} + \sum_{I \neq J} \frac{Z_I Z_J}{2|R_I - R_J|} + \sum_{I,k} \frac{Z_I}{2|R_I - r_k|} - \sum_{k \neq k'} \frac{1}{2|r_k - r'_k|}
\]

\[ \Psi \equiv \Psi(\{R_I\}, \{r_k\}) \]

All coordinates coupled.
Actually, difficult to even ignore time dependence if electrons and nuclei treated together outrightly.
We Have a Predictive Theory for (Almost) Everything!

\[
\hat{\mathcal{H}}\Psi = E\Psi
\]

Dirac 1929:
“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known ...”

“... and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

\[
\hat{\mathcal{H}} = \sum_I \frac{P_I^2}{2M_I} + \sum_k \frac{p_k^2}{2m_e} + \sum_{I \neq J} \frac{Z_I Z_J}{2|R_I - R_J|} + \sum_{I,k} \frac{Z_I}{2|R_I - r_k|} - \sum_{k \neq k'} \frac{1}{2|r_k - r'_k|}
\]

\[
\Psi \equiv \Psi(\{R_I\}, \{r_k\})
\]

All coordinates coupled.

Actually, difficult to even ignore time dependence if electrons and nuclei treated together outrightly.
We Have a Predictive Theory for (Almost) Everything!

\[ \hat{\mathcal{H}} \Psi = E \Psi \]

Dirac 1929:

“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known …”

“… and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

“… it therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.”

Standard Steps to “Practical” Electronic Structure Theory

1) Separate Electron and Nuclear Coordinates (Born-Oppenheimer Approximation)

2) Address the electronic problem:

\[ \sum_k \frac{p_k^2}{2m_e} + \sum_{I,k} \frac{Z_I}{2|R_I - r_k|} - \sum_{k \neq k'} \frac{1}{2|r_k - r'_k|} \]

\[ \hat{H}_{el} \Phi(\{R_I\}, \{r_k\}) = E(\{R_I\}) \cdot \Phi(\{R_I\}, \{r_k\}) \]

This talk: Focus on solution of the electronic problem.
Current “workhorse” electronic structure theory

Quantum chemistry & many-body theory:

\[ E_{\text{tot}} \leq \langle \psi | H | \psi \rangle \quad \text{... successive refinement of } \psi \]
Current “workhorse” electronic structure theory

Quantum chemistry & many-body theory:

\[ E_{\text{tot}} \leq \langle \psi | H | \psi \rangle \]

... successive refinement of \( \Psi \)

Density functional theory: (Hohenberg-Kohn 1964, Kohn-Sham 1965)

\[ E_{\text{tot}} = E[n(r)] = T_s[n] + V[n] + V_{es}[n] + E_{xc}[n] \]
Current “workhorse” electronic structure theory

Quantum chemistry & many-body theory:

\[ E_{\text{tot}} \leq \langle \psi | H | \psi \rangle \]

... successive refinement of \( \psi \)

Density functional theory: (Hohenberg-Kohn 1964, Kohn-Sham 1965)

\[ E_{\text{tot}} = E[n(r)] = T_s[n] + V[n] + V_{es}[n] + E_{\text{xc}}[n] \]

• Key practical approximation: \( E_{\text{xc}} \)
Current “workhorse” electronic structure theory

Quantum chemistry & many-body theory:

\[ E_{\text{tot}} \leq \langle \psi | H | \psi \rangle \]

... successive refinement of \( \psi \)

Density functional theory: (Hohenberg-Kohn 1964, Kohn-Sham 1965)

\[ E_{\text{tot}} = E[n(r)] = T_s[n] + V[n] + V_{\text{es}}[n] + E_{\text{xc}}[n] \]

“Perdew’s ladder” to exact solution

• Key practical approximation: \( E_{\text{xc}} \)
  
  response / many-body terms: GW, RPA, SOSEX, ...
  
  hybrid functionals: non-local exchange
  
  meta-GGAs: \( \nabla^2 n(r), \nabla^2 \phi(r) \)
  
  Generalized gradient approximations (GGAs): \( |\nabla n(r)| \)
  
  Local-density approximation (LDA): \( n(r) \)
Current “workhorse” electronic structure theory

Quantum chemistry & many-body theory:

\[ E_{\text{tot}} \leq \langle \psi | H | \psi \rangle \]

... successive refinement of \( \psi \)

Density functional theory: (Hohenberg-Kohn 1964, Kohn-Sham 1965)

\[ E_{\text{tot}} = E[n(r)] = T_s[n] + V[n] + V_{\text{es}}[n] + E_{\text{xc}}[n] \]

“Perdew’s ladder” to exact solution

- Key practical approximation: \( E_{\text{xc}} \)
- Response / many-body terms: GW, RPA, SOSEX, ...
- Hybrid functionals: non-local exchange
- Meta-GGAs: \( \nabla^2 n(r), \nabla^2 \phi(r) \)
- Generalized gradient approximations (GGAs): \( |\nabla n(r)| \)
- Local-density approximation (LDA): \( n(r) \)
- + van der Waals
In 2004, we began a new electronic structure code...

Universality: Cover full space of materials and chemistry
In 2004, We Began a New Electronic Structure Code ...

Universality: Cover full space of materials and chemistry

“Materials and molecules” - periodic (k-space) and non-periodic
In 2004, We Began a New Electronic Structure Code ...

Universality:  Cover full space of materials and chemistry
   “Materials and molecules” - periodic (k-space) and non-periodic

Accuracy:   Hierarchy of methods: DFT and “beyond” (GW, MP2, RPA, rPT2, ...)
   All-electron
In 2004, We Began a New Electronic Structure Code...

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period</td>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>Li</td>
<td>Be</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Na</td>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>Ar</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
<td>Xe</td>
</tr>
<tr>
<td>5</td>
<td>Cs</td>
<td>Ba</td>
<td></td>
<td>Hf</td>
<td>Ta</td>
<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
<td>Rn</td>
</tr>
<tr>
<td>6</td>
<td>Fr</td>
<td>Ra</td>
<td></td>
<td>Rf</td>
<td>Db</td>
<td>Sg</td>
<td>Bh</td>
<td>Hs</td>
<td>Mt</td>
<td>Ds</td>
<td>Rg</td>
<td>Cn</td>
<td>Uut</td>
<td>Fl</td>
<td>Uup</td>
<td>Lve</td>
<td>Uus</td>
<td>Uuo</td>
</tr>
</tbody>
</table>

**Universality:** Cover full space of materials and chemistry  
“Materials and molecules” - periodic (k-space) and non-periodic

**Accuracy:** Hierarchy of methods: DFT and “beyond” (GW, MP2, RPA, rPT2, ...)

**All-electron**

**Efficiency:** Scalable (system size, number of CPUs)
In 2004, we began a new electronic structure code ... 

Universality: Cover full space of materials and chemistry  
“Materials and molecules” - periodic (k-space) and non-periodic

Accuracy: Hierarchy of methods: DFT and “beyond” (GW, MP2, RPA, rPT2, ...)  
All-electron

Efficiency: Scalable (system size, number of CPUs)

Efficient (1,000s of atoms), but do not sacrifice accuracy!
Central Decision: How to Discretize the Problem?

\[
\begin{bmatrix}
-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \\
\end{bmatrix} \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})
\]

“Basis set expansion”:

\[
\psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})
\]

Kohn, Sham 1965
Central Decision: How to Discretize the Problem?

\[
\begin{pmatrix}
-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})
\end{pmatrix} \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r})
\]

“Basis set expansion”:
\[
\psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})
\]

Generalized eigenvalue problem:
\[
\hbar c_k = \epsilon_k S c_k
\]

\[
h_{ij} = \langle \varphi_i | \hat{h}_{\text{KS}} | \varphi_j \rangle
\]

\[
s_{ij} = \langle \varphi_i | \varphi_j \rangle
\]
Central Decision: How to Discretize the Problem?

“Basis set expansion”:
\[
\psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r})
\]

Generalized eigenvalue problem:
\[
\begin{bmatrix}
-\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})
\end{bmatrix}
\psi_k(\mathbf{r}) = \varepsilon_k \psi_k(\mathbf{r})
\]

Many good options:
- Plane waves (VASP, abinit, ...)

Kohn, Sham 1965

\[
\varphi_k(\mathbf{r}) = \frac{1}{N} e^{ikr}
\]
Central Decision: How to Discretize the Problem?

"Basis set expansion":

\[ \psi_k(r) = \sum_i c_{ki} \varphi_i(r) \]

Generalized eigenvalue problem:

\[ \hat{h} c_k = \epsilon_k s_k c_k \]

\[ h_{ij} = \langle \varphi_i | \hat{h}_{KS} | \varphi_j \rangle \]

\[ s_{ij} = \langle \varphi_i | \varphi_j \rangle \]

Many good options:

- Plane waves (VASP, abinit, ...)

\[ \varphi_k(r) = \frac{1}{N} e^{ikr} \]

- Gaussian-type orbitals

\[ \varphi_{lmn}(r) = \frac{1}{N} x^l y^m z^n e^{-\alpha r^2} \]

Kohn, Sham 1965

\[ \begin{bmatrix} -\frac{\nabla^2}{2} + v_{\text{ext}}(r) + v_{\text{es}}(r) + v_{\text{xc}}(r) \end{bmatrix} \psi_k(r) = \epsilon_k \psi_k(r) \]
Central Decision: How to Discretize the Problem?

\[ \frac{-\nabla^2}{2} + v_{\text{ext}}(\mathbf{r}) + v_{\text{es}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}) \]

Kohn, Sham 1965

“Basis set expansion”:

\[ \psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r}) \]

Generalized eigenvalue problem:

\[ \hbar c_k = \epsilon_k s c_k \]

\[ h_{ij} = \langle \varphi_i | \hat{h}_{\text{KS}} | \varphi_j \rangle \]

\[ s_{ij} = \langle \varphi_i | \varphi_j \rangle \]

Many good options:

• Plane waves (VASP, abinit, ...)

\[ \varphi_k(\mathbf{r}) = \frac{1}{N} e^{i k r} \]

• Gaussian-type orbitals

\[ \varphi_{lmn}(\mathbf{r}) = \frac{1}{N} x^l y^m z^n e^{-\alpha r^2} \]

• Many others: “Augmented plane waves”,
  wavelets, finite elements,
  numeric atom-centered functions, ...

Our choice!

\[ \varphi_{i[lm]}(\mathbf{r}) = \frac{u_i(r)}{r} \cdot Y_{lm}(\Omega) \]
Central Decision: How to Discretize the Problem?

\[ -\frac{\nabla^2}{2} + \nu_{\text{ext}}(\mathbf{r}) + \nu_{\text{es}}(\mathbf{r}) + \nu_{\text{xc}}(\mathbf{r}) \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}) \]

**“Basis set expansion”:**

\[ \psi_k(\mathbf{r}) = \sum_i c_{ki} \varphi_i(\mathbf{r}) \]

**Generalized eigenvalue problem:**

\[ \hat{h} c_k = \epsilon_k s c_k \]

\[ h_{ij} = \langle \varphi_i | \hat{h}_{\text{KS}} | \varphi_j \rangle \]

\[ s_{ij} = \langle \varphi_i | \varphi_j \rangle \]

Many good options:

- **Plane waves** \((\text{VASP, abinit, ...})\)
  
  \[ \varphi_k(\mathbf{r}) = \frac{1}{N} e^{ikr} \]

  **X. Gonze**
  Wed 10:00h

- **Gaussian-type orbitals**
  
  \[ \varphi_{lmn}(\mathbf{r}) = \frac{1}{N} x^l y^m z^n e^{-\alpha r^2} \]

  **I.Y. Zhang**
  Thu 10:00h

- **Many** others: “Augmented plane waves”, wavelets, finite elements, numeric atom-centered functions, ...

  **S. Goedecker**
  Tue(2) 9:00h

Our choice!

\[ \varphi_{l|mn}(\mathbf{r}) = \frac{u_i(\mathbf{r})}{r} \cdot Y_{lm}(\Omega) \]
Our Choice: Numeric Atom-Centered Basis Functions

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

- \( u_i(r) \): Flexible choice - “Anything you like.”

Many popular implementations:
- DMol³ (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.),
- PAOs (Siesta, Conquest, OpenMX², Fireball, ...
Our Choice: Numeric Atom-Centered Basis Functions

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

• \( u_i(r) \): Flexible choice - “Anything you like.”

\[
\begin{bmatrix}
-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}}(r)
\end{bmatrix} u_i(r) = \epsilon_i u_i(r)
\]

Many popular implementations: DMol\(^3\) (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX\(^2\), Fireball, ...)
Our Choice: Numeric Atom-Centered Basis Functions

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

- \( u_i(r) \): Flexible choice - “Anything you like.”

- free-atom like: \( v_i(r) = v_{\text{DFT}}^{\text{free atom}}(r) \)

- Hydrogen-like: \( v_i(r) = z/r \)

- free ions, harm. osc. (Gaussians), ...

Many popular implementations:
DMol³ (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX², Fireball, ...)

\[ \left[ -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + v_i(r) + v_{\text{cut}}(r) \right] u_i(r) = \varepsilon_i u_i(r) \]
Our Choice: Numeric Atom-Centered Basis Functions

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

- \(u_i(r)\): Flexible choice - “Anything you like.”

\[
\begin{align*}
- \frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l + 1)}{r^2} + v_i(r) + v_{\text{cut}}(r) & \quad \Rightarrow \quad u_i(r) = \epsilon_i u_i(r)
\end{align*}
\]

- free-atom like: \(v_i(r) = v_{\text{DFT}}^\text{free atom}(r)\)
- Hydrogen-like: \(v_i(r) = z/r\)
- free ions, harm. osc. (Gaussians), ...

Many popular implementations:
DMol³ (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX², Fireball, ...)

u(r) (cutoff pot'l)
Our Choice: Numeric Atom-Centered Basis Functions

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

- \( u_i(r) \): Flexible choice - “Anything you like.”

- Localized; ”naturally” all-electron

- The choice of efficient and of enough radial functions is obviously important

- We have a basis set library for all elements (1-102), from fast qualitative to meV-converged total energies (LDA/GGA/hybrid DF’s) - efficient and accurate approach

Many popular implementations: DMol\(^3\) (Delley), FPLO (Eschrig et al.), PLATO (Horsfield et al.), PAOs (Siesta, Conquest, OpenMX\(^2\), Fireball, ...)

Example: Hierarchical Basis Set Library for All Elements

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>O</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimal</td>
<td>1s</td>
<td>[He]+2s2p</td>
<td>[He]+2s2p</td>
<td>[Xe]+6s5d4f</td>
</tr>
<tr>
<td>Tier 1</td>
<td>H(2s,2.1)</td>
<td>H(2p,1.7)</td>
<td>H(2p,1.8)</td>
<td>Au²⁺(6p)</td>
</tr>
<tr>
<td></td>
<td>H(2p,3.5)</td>
<td>H(3d,6.0)</td>
<td>H(3d,7.6)</td>
<td>H(4f,7.4)</td>
</tr>
<tr>
<td></td>
<td>H(2s,4.9)</td>
<td>H(3s,6.4)</td>
<td>Au²⁺(6s)</td>
<td>H(5g,10)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(6h,12.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(3d,2.5)</td>
</tr>
<tr>
<td>Tier 2</td>
<td>H(1s,0.85)</td>
<td>H(4f,9.8)</td>
<td>H(4f,11.6)</td>
<td>H(5f,14.8)</td>
</tr>
<tr>
<td></td>
<td>H(2p,3.7)</td>
<td>H(3p,5.2)</td>
<td>H(3p,6.2)</td>
<td>H(4d,3.9)</td>
</tr>
<tr>
<td></td>
<td>H(2s,1.2)</td>
<td>H(3s,4.3)</td>
<td>H(3d,5.6)</td>
<td>H(3p,3.3)</td>
</tr>
<tr>
<td></td>
<td>H(3d,7.0)</td>
<td>H(5g,14.4)</td>
<td>H(5g,17.6)</td>
<td>H(1s,0.45)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(3d,6.2)</td>
<td>H(1s,0.75)</td>
<td>H(5g,16.4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H(6h,13.6)</td>
</tr>
<tr>
<td>Tier 3</td>
<td>H(4f,11.2)</td>
<td>H(2p,5.6)</td>
<td>O²⁺(2p)</td>
<td>H(4f,5.2)*</td>
</tr>
<tr>
<td></td>
<td>H(3p,4.8)</td>
<td>H(2s,1.4)</td>
<td>H(4f,10.8)</td>
<td>H(4d,5.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>...</td>
</tr>
</tbody>
</table>

Systematic hierarchy of basis (sub)sets, iterative *automated* construction based on *dimers*

“First tier (level)”

“Second tier”

“Third tier”
Accuracy: \((\text{H}_2\text{O})_2\) Hydrogen Bond Energy

\[ \text{Basis set limit (independent): } E_{\text{Hb}} = -219.8 \text{ meV} \]

<table>
<thead>
<tr>
<th>Basis sets: Radial fn. character</th>
<th>H</th>
<th>C,N,O</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimal</td>
<td>1s</td>
<td>[He]+2s2p</td>
</tr>
<tr>
<td>tier 1</td>
<td>s,p</td>
<td>s,p,d</td>
</tr>
<tr>
<td>tier 2</td>
<td>s,p,s,d</td>
<td>s,p,d,f,g</td>
</tr>
<tr>
<td>tier 3</td>
<td>s,p,d,f</td>
<td>s,p,d,f</td>
</tr>
</tbody>
</table>

\[ \text{H}_2\text{O}-\text{H}_2\text{O} \text{ binding energy [eV]} \]

\[ \text{Basis size} \]
Accuracy in Community Wide Benchmark - “Delta Test”

https://molmod.ugent.be/deltacodesdft

$E(V)$ for 71 elemental solids - 15 codes, all-electron & 40 pseudopot’l sets

\[
\Delta_i(a, b) = \sqrt{\int_{0.94V_0,i}^{1.06V_0,i} \frac{(E_{b,i}(V) - E_{a,i}(V))^2}{0.12V_0,i} \, dV}
\]
Accuracy in Community Wide Benchmark - “Delta Test”

https://molmod.ugent.be/deltacodesdft

E(V) for 71 elemental solids - 15 codes, all-electron & 40 pseudopot’l sets

FHI-aims: Test carried out independently by Dr. Marcin Dulak, DTU (Copenhagen)
Accuracy in Community Wide Benchmark - “Delta Test”

https://molmod.ugent.be/deltacodesdft

<table>
<thead>
<tr>
<th>Code</th>
<th>Basis</th>
<th>Electron treatment</th>
<th>Delta (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wien2k 13.1</td>
<td>LAPW/APW+lo</td>
<td>All-electron</td>
<td>0</td>
</tr>
<tr>
<td>FHI-aims 081213*</td>
<td>NAO, tier2</td>
<td>All-electron (scalar rel. atomic ZORA)</td>
<td>0.2</td>
</tr>
<tr>
<td>Exciting (dev.)</td>
<td>LAPW+xlo</td>
<td>All-electron</td>
<td>0.2</td>
</tr>
<tr>
<td>Quantum Espresso 5.1</td>
<td>plane waves</td>
<td>SSSP accuracy (mixed NC/US/PAW library)</td>
<td>0.3</td>
</tr>
<tr>
<td>VASP 5.2.12</td>
<td>plane waves</td>
<td>PAW 2015</td>
<td>0.3</td>
</tr>
<tr>
<td>FHI-aims 081213*</td>
<td>NAO, tier2</td>
<td>All-electron (scalar rel., scaled ZORA)</td>
<td>0.3</td>
</tr>
<tr>
<td>ELK 3.1.5</td>
<td>APW+lo</td>
<td>All-electron</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Results: Marcin Dulak, DTU (Copenhagen)
Total Energy Benchmark at the Absolute Basis Set Limit

“The Elephant in the Room of Density Functional Theory”
Stig Rune Jensen, Santanu Saha, Jose A. Flores-Livas, William Huhn, Volker Blum, Stefan Goedecker, Luca Frediani

Benchmark of different basis set types vs. multiresolution wavelets ($\mu$Ha accuracy)
Reference: 211 molecules, elements 1-18
Total and Atomization Energies vs. an Absolute Reference

Reference: “MRChem”
Multiresolution wavelets
(μHa accuracy)

Benchmark:
211 molecules,
elements 1-18
DFT-LDA, PBE, PBE0

DFT-PBE
Total and Atomization Energies vs. an Absolute Reference

Reference: “MRChem”
Multiresolution wavelets (μHa accuracy)

Benchmark:
211 molecules, elements 1-18
DFT-LDA, PBE, PBE0

FHI-aims/Light
FHI-aims/Tight
FHI-aims/Tier2
FHI-aims/Tier4
aug-cc-pVDZ
aug-cc-pVTZ
aug-cc-pVQZ
aug-cc-pV5Z
Total and Atomization Energies vs. an Absolute Reference

Reference: “MRChem”
Multiresolution wavelets (μHa accuracy)

Benchmark:
211 molecules,
elements 1-18
DFT-LDA, PBE, PBE0

Stig Rune Jensen, Santanu Saha, Jose A. Flores-Livas, William Huhn, Volker Blum, Stefan Goedecker, Luca Frediani

DFT-PBE

FHI-aims/Light
FHI-aims/Tight
FHI-aims/Tier2
FHI-aims/Tier4
aug-cc-pVDZ
aug-cc-pVTZ
aug-cc-pVQZ
aug-cc-pV5Z
Similar High Precision Achievable for Band Structures

Using Numeric Atom-Centered Basis Functions: Pieces

- **Numerical Integration**
  \[ h_{ij} = \int d^3 r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

- **Electron density update**
  \[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

- **All-electron electrostatics**
  \[ \nu_{es}(r) = \int d^3 r' \frac{n(r')}{|r - r'|} \]

- **Relativity**
  needed for heavy elements

- **Eigenvalue solver**
  \[ \hbar c_k = \epsilon_k \bar{s} c_k \]

- **Periodic systems**
  need suitable basis,
  Coulomb Operator

- **Coulomb operator**
  \[ \langle ij|kl \rangle = \int d^3 r d^3 r' \frac{\varphi_i(r) \varphi_j(r') \varphi_k(r) \varphi_l(r')}{|r - r'|} \]
Using Numeric Atom-Centered Basis Functions: Pieces

- **Numerical Integration**
  \[ h_{ij} = \int d^3 r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

- **Electron density update**
  \[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

- **All-electron electrostatics**
  \[ v_{es}(r) = \int d^3 r' \frac{n(r')}{|r - r'|} \]

- **Relativity**
  needed for heavy elements

- **Eigenvalue solver**
  \[ \frac{\hbar}{m} c_k = \epsilon_k \frac{s}{m} c_k \]

- **Periodic systems**
  need suitable basis,
  Coulomb Operator

- **Coulomb operator**
  \[ (i j | k l) = \int d^3 r d^3 r' \frac{\varphi_i(r) \varphi_j(r') \varphi_k(r) \varphi_l(r')}{|r - r'|} \]
Numeric Atom-Centered Basis Functions: Integration

\[ h_{ij} = \int d^3r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

- Discretize to integration grid: \( \int d^3r f(r) \rightarrow \sum_r w(r) f(r) \)

... but even-spaced integration grids are out: \( f(r) \) strongly peaked near all nuclei!
Numeric Atom-Centered Basis Functions: Integration

\[ h_{ij} = \int d^3 r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

- **Discretize to integration grid:**
  \[ \int d^3 r f(r) \rightarrow \sum_r w(r) f(r) \]

  ... but even-spaced integration grids are out: \( f(r) \) strongly peaked near all nuclei!

- **Overlapping atom-centered integration grids:**
  - Radial shells (e.g., H, light: 24; Au, tight: 147)
  - Specific angular point distribution (“Lebedev”) exact up to given integration order \( l \) (50, 110, 194, 302, ... points per shell)

Pioneered by
Becke JCP 88, 2547 (1988), Delley, JCP 92, 508 (1990), MANY others!
Overlapping Atom-Centered Grids: “Partitioning of Unity”

\[ h_{ij} = \int d^3r \varphi_i(r) \hat{h}_{\text{KS}} \varphi_j(r) \]

- Rewrite to atom-centered integrands:

\[ \int d^3r f(r) = \sum_{\text{atoms}} \int d^3r p_{\text{atom}}(r) f(r) \]

**exact:** \[ \sum_{\text{atoms}} p_{\text{atom}}(r) = 1 \]

**through** \[ p_{\text{atom}}(r) = \frac{g_{\text{atom}}(r)}{\sum_{\text{atom'}} g_{\text{atom'}}(r)} \]
Overlapping Atom-Centered Grids: “Partitioning of Unity”

\[ h_{ij} = \int d^3 r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

- Rewrite to atom-centered integrands:

\[ \int d^3 r f(r) = \sum_{\text{atoms}} \int d^3 r p_{\text{atom}}(r) f(r) \]

**exact:** \( \sum_{\text{atoms}} p_{\text{atom}}(r) = 1 \)

**through** \( p_{\text{atom}}(r) = \frac{g_{\text{atom}}(r)}{\sum_{\text{atom'}} g_{\text{atom'}}(r)} \)

- e.g.: \( g_{\text{atom}} = \frac{\rho_{\text{atom}}(r)}{r^2} \) (Delley 1990)

many alternatives:
Becke 1988, Stratmann 1996, Koepernik 1999, ...
Integration in Practice: Large Systems, Small Errors!

Fully extended Polyalanine peptide molecule Ala$_{20}$, DFT-PBE (203 atoms)

Integration error

Total energy error [eV]

Integration points per radial shell

$g_{at}(r)$: Delley 1990

$g_{at}(r)$: Stratmann et al. 1996
Hartree Potential (Electrostatics): Overlapping Multipoles

\[ v_{es}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

- Partitioning of Unity:
  
  \[ n(r) = \sum_{\text{atoms}} p_{\text{atom}}(r)n(r) \]

Becke 1988
Delley 1990

(same trick as used for integrals)
Hartree Potential (Electrostatics): Overlapping Multipoles

\[ v_{es}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

- **Partitioning of Unity:**
  
  \[ n(r) = \sum_{\text{atoms}} p_{\text{atom}}(r)n(r) \]

- **Multipole expansion:**
  
  \[ n_{\text{atom,lm}}(r) = \int_{s=|r' - R_{\text{atom}}|} p_{\text{atom}}(r')n(r')Y_{lm}(\Omega) \]

*Becke 1988
Delley 1990*
Hartree Potential (Electrostatics): Overlapping Multipole

\[ v_{es}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

- **Partitioning of Unity:**
  \[ n(r) = \sum_{\text{atoms}} p_{\text{atom}}(r)n(r) \]

  *Becke 1988, Delley 1990*

- **Multipole expansion:**
  \[ n_{\text{atom,lm}}(r) = \int_{s=|r' - R_{\text{atom}}|} p_{\text{atom}}(r')n(r')Y_{lm}(\Omega) \]

- **Classical electrostatics:**
  \[ v_{es}(r) = \sum_{\text{atoms}} \sum_{lm} v_{\text{atom,lm}}(|r - R_{\text{atom}}|)Y_{lm}(\Omega_{\text{atom}}) \]
Electrostatics: Multipole expansion

\[ v_{es}(\mathbf{r}) = \sum_{\text{atoms}} \sum_{lm} v_{\text{atom},lm}(|\mathbf{r} - \mathbf{R}_{\text{atom}}|) Y_{lm}(\Omega_{\text{atom}}) \]

Polyalanine Ala\textsubscript{20}, DFT-PBE (203 atoms)

\(\alpha\)-helical vs. extended: Total energy convergence with \(l_{\text{max}}\)

\[ E_{\text{tot}}(\alpha \text{ helix}) \]

\[ E_{\text{tot}}(\text{extended}) \]

Energy difference

Maximum angular momentum \(l\) in multipole expansion

\(\alpha\)-helical vs. extended
Using Numeric Atom-Centered Basis Functions: Pieces

• **Numerical Integration**
  \[ h_{ij} = \int d^3r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

• **Electron density update**
  \[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

• **All-electron electrostatics**
  \[ v_{es}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

• **Relativity**
  *needed for heavy elements*

• **Eigenvalue solver**
  \[ \hbar c_k = \epsilon_k \sum_c c_k \]

• **Periodic systems**
  *need suitable basis, Coulomb Operator*

• **Coulomb operator**
  \[ (ij|kl) = \int d^3r d^3r' \frac{\varphi_i(r) \varphi_j(r') \varphi_k(r) \varphi_l(r')}{|r - r'|} \]
Using Numeric Atom-Centered Basis Functions: Pieces

• **Numerical Integration**
  \[ h_{ij} = \int d^3r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

• **Electron density update**
  \[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

• **All-electron electrostatics**
  \[ v_{es}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

• **Relativity**
  needed for heavy elements

• **Eigenvalue solver**
  \[ \hbar \sigma_k = \epsilon_k \sigma_k \]

• **Periodic systems**
  need suitable basis,
  Coulomb Operator

• **Coulomb operator**
  \[ (ij|kl) = \int d^3rd^3r' \frac{\varphi_i(r)\varphi_j(r')\varphi_k(r)\varphi_l(r')}{|r - r'|} \]
Spin-Orbit Coupling in Zincblende GaAs
Essential for correct carrier properties - even for relatively light material.
Must account for independently of “functional.”

\[ \sigma_{\text{exp}} = 5.6532 \, \text{Å} \]

How Strong are Relativistic Effects Across the Periodic Table?

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Li</td>
<td>Be</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>Na</td>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>Rb</td>
<td>Sr</td>
<td>Y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>Cs</td>
<td>Ba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>87</td>
<td>Fr</td>
<td>Ra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lanthanides</td>
<td>57</td>
<td>La</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actinides</td>
<td>89</td>
<td>Ac</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

William Huhn  
(Duke Univ.)
How Strong are Relativistic Effects Across the Periodic Table?

<table>
<thead>
<tr>
<th>Group Period</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 H</td>
<td>3 Li</td>
<td>4 Be</td>
<td>11 Na</td>
<td>12 Mg</td>
<td>19 K</td>
<td>20 Ca</td>
<td>21 Sc</td>
<td>22 Ti</td>
<td>23 V</td>
<td>24 Cr</td>
<td>25 Mn</td>
<td>26 Fe</td>
<td>27 Co</td>
<td>28 Ni</td>
<td>29 Cu</td>
<td>30 Zn</td>
<td>31 Ga</td>
<td>32 Ge</td>
</tr>
<tr>
<td>2 GaAs: Moderate</td>
<td>Pb: Heavy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Rb</td>
<td>38 Sr</td>
<td>39 Y</td>
<td>40 Zr</td>
<td>41 Nb</td>
<td>42 Mo</td>
<td>43 Tc</td>
<td>44 Ru</td>
<td>45 Rh</td>
<td>46 Pd</td>
<td>47 Ag</td>
<td>48 Cd</td>
<td>49 In</td>
<td>50 Sn</td>
<td>51 Sb</td>
<td>52 Te</td>
<td>53 I</td>
<td>54 Xe</td>
<td></td>
</tr>
<tr>
<td>4 Cs</td>
<td>56 Ba</td>
<td>55 La</td>
<td>57 Ce</td>
<td>58 Pr</td>
<td>59 Nd</td>
<td>60 Pm</td>
<td>61 Sm</td>
<td>62 Eu</td>
<td>63 Tm</td>
<td>64 Dy</td>
<td>65 Ho</td>
<td>66 Er</td>
<td>67 Hg</td>
<td>68 Tl</td>
<td>69 Pb</td>
<td>70 Bi</td>
<td>71 Po</td>
<td></td>
</tr>
<tr>
<td>5 Fr</td>
<td>88 Ra</td>
<td>87 Th</td>
<td>86 Pb</td>
<td>85 Bi</td>
<td>84 Po</td>
<td>83 At</td>
<td>82 Rn</td>
<td>81 Fr</td>
<td>80 Re</td>
<td>79 Os</td>
<td>78 Ir</td>
<td>77 Pt</td>
<td>76 Rh</td>
<td>75 Pd</td>
<td>74 Au</td>
<td>73 Hf</td>
<td>72 Ta</td>
<td>71 W</td>
</tr>
<tr>
<td>Lanthanides</td>
<td>57 La</td>
<td>58 Ce</td>
<td>59 Pr</td>
<td>60 Nd</td>
<td>61 Pm</td>
<td>62 Sm</td>
<td>63 Eu</td>
<td>64 Gd</td>
<td>65 Tb</td>
<td>66 Dy</td>
<td>67 Ho</td>
<td>68 Er</td>
<td>69 Tm</td>
<td>70 Yb</td>
<td>71 Lu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actinides</td>
<td>89 Ac</td>
<td>90 Th</td>
<td>91 Pa</td>
<td>92 U</td>
<td>93 Np</td>
<td>94 Pu</td>
<td>95 Am</td>
<td>96 Cm</td>
<td>97 Bk</td>
<td>98 Cf</td>
<td>99 Es</td>
<td>100 Fm</td>
<td>101 Md</td>
<td>102 No</td>
<td>103 Lr</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Non-relativistic QM: Schrödinger Equation

\[ V\phi + \frac{p^2}{2m} \phi = \epsilon \phi \]

- one component (two with spin)
- one Hamiltonian for all states
Relativity

Non-relativistic QM: Schrödinger Equation

\[ V \phi + \frac{p^2}{2m} \phi = \epsilon \phi \]

- one component
  (two with spin)
- one Hamiltonian for all states

Relativistic QM: Dirac Equation

\[
\begin{pmatrix}
V & c \sigma \cdot p \\
 c \sigma \cdot p & -2c^2 + V
\end{pmatrix}
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix} = \epsilon
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix}
\]
Relativity

Non-relativistic QM: Schrödinger Equation

\[ V\phi + \frac{p^2}{2m}\phi = \epsilon\phi \]

- one component
- (two with spin)
- one Hamiltonian for all states

Relativistic QM: Dirac Equation

\[
\begin{pmatrix}
V & c\sigma \cdot p \\
c\sigma \cdot p & -2c^2 + V
\end{pmatrix}
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix}
= \epsilon
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix}
\]

- \(\epsilon\)-dependent Hamiltonian
- Not negligible for \(\epsilon - v(r) \approx 2c^2\)
- \(\approx\) affects near-nuclear part of any wave function
Relativity

Non-relativistic QM: Schrödinger Equation

\[ V\phi + \frac{p^2}{2m}\phi = \epsilon\phi \]

- one component (two with spin)
- one Hamiltonian for all states

Relativistic QM: Dirac Equation

\[
\begin{pmatrix}
V & c\sigma \cdot p \\
c\sigma \cdot p & -2c^2 + V
\end{pmatrix}
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix}
= \epsilon
\begin{pmatrix}
\phi \\
\chi
\end{pmatrix}
\]

- \(\epsilon\)-dependent Hamiltonian
- Not negligible for \(\epsilon \approx 2c^2\)
  \(\leftarrow\) affects near-nuclear part of any wave function

... simply rewrite:

\[ V\phi + \sigma \cdot p \frac{c^2}{2c^2 + \epsilon - V} \sigma \cdot p\phi = \epsilon\phi \]

Common first step: Ignore Pauli matrices \(\sigma_i\) \(\leftrightarrow\) neglect spin-orbit coupling.
Simple Approximation to Scalar Relativity

\[ V\phi + p \frac{c^2}{2c^2 + \epsilon - V} p\phi = \epsilon\phi \]

1. LAPW, others: Outright treatment
   → radial functions in atomic sphere (core, valence): Per-state relativistic
   → 3-dimensional non-relativistic treatment of interstitial regions
   Tricky with NAO’s: Basis functions from different atomic centers overlap!

2. Approximate one-Hamiltonian treatment
   Popular: Zero-order regular approximation (ZORA) [1]

1. LAPW, others: Outright treatment
   → radial functions in atomic sphere (core, valence): Per-state relativistic
   → 3-dimensional non-relativistic treatment of interstitial regions
   Tricky with NAO’s: Basis functions from different atomic centers overlap!

2. Approximate one-Hamiltonian treatment
   Popular: Zero-order regular approximation (ZORA) [1]
   ... not gauge-invariant!

Simple Approximation to Scalar Relativity

1. LAPW, others: Outright treatment
   - radial functions in atomic sphere (core, valence): Per-state relativistic
   - 3-dimensional non-relativistic treatment of interstitial regions
   - Tricky with NAO's: Basis functions from different atomic centers overlap!

2. Approximate one-Hamiltonian treatment
   - Popular: Zero-order regular approximation (ZORA) [1]

   \[ V\phi + \frac{p^2}{2m} + \frac{c^2}{2} \nabla p \phi = \epsilon \phi \]

   ZORA in practice: Harsh approximation (known)

   Au dimer - LDA

   Nonrel.:
   - LAPW
   - FHI-aims

   Relativistic:
   - LAPW
   - ZORA

Fixing ZORA: “Atomic ZORA”

\[ V \phi + p \frac{c^2}{2c^2 + \nabla - V} p \phi = \epsilon \phi \]

\(^1\text{CPC 180, 2175 (2009);}^2\text{Science 351, aad3000 (2016);}^3\text{arXiv:1705.01804 (2017)}\)
Fixing ZORA: “Atomic ZORA”

\[ V \phi + p \frac{c^2}{2c^2 + V} p \phi = \epsilon \phi \]

“Atomic ZORA”\(^1\)

\[ V \phi + p \frac{c^2}{2c^2 - V_{\text{free atom}}} p \phi = \epsilon \phi \]

- No gauge-invariance problem
- Simple total-energy gradients
- Accurate energy differences\(^2\)
- Accurate scalar-relativistic valence & conduction eigenvalues\(^3\)

\(^1\)CPC 180, 2175 (2009); \(^2\)Science 351, aad3000 (2016); \(^3\)arXiv:1705.01804 (2017)
Fixing ZORA: “Atomic ZORA”

\[ V\phi + p\frac{c^2}{2c^2 + V}p\phi = \epsilon\phi \]

- No gauge-invariance problem
- Simple total-energy gradients
- Accurate energy differences
- Accurate scalar-relativistic valence & conduction eigenvalues

1 CPC 180, 2175 (2009); 2 Science 351, aad3000 (2016); 3 arXiv:1705.01804 (2017)
Now How About Spin-Orbit Coupling?

Common first step: Ignore Pauli matrices $\sigma_i \leftrightarrow$ neglect spin-orbit coupling.
Now How About Spin-Orbit Coupling?

\[ V\phi + \sigma \cdot \mathbf{p} \frac{c^2}{2c^2 + \epsilon - V} \sigma \cdot \mathbf{p}\phi = \epsilon\phi \]

\[ \sigma_1 = \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]
Now How About Spin-Orbit Coupling?

\[ V\phi + \sigma \cdot p \frac{c^2}{2c^2 + \epsilon - V} \sigma \cdot p\phi = \epsilon\phi \]

\[ \sigma_1 = \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_2 = \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_3 = \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \]

Rewrite (exact):

\[ V\phi + \left( p \frac{c^2}{2c^2 + \epsilon - V} p + ip \frac{c^2}{2c^2 + \epsilon - V} \times p \cdot \sigma \right)\phi = \epsilon\phi \]
Now How About Spin-Orbit Coupling?

\[ V\phi + \sigma \cdot p \frac{c^2}{2c^2 + \epsilon - V} \sigma \cdot p\phi = \epsilon\phi \]

\[
\begin{align*}
\sigma_1 &= \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\
\sigma_2 &= \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \\
\sigma_3 &= \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}
\end{align*}
\]

Rewrite (exact):

\[ V\phi + \left(p \frac{c^2}{2c^2 + \epsilon - V} p + i p \frac{c^2}{2c^2 + \epsilon - V} \times p \cdot \sigma \right)\phi = \epsilon\phi \]

e.g., atomic ZORA

\[ H_{SOC} = \frac{i}{4c^2} pV \times p \cdot \sigma \]

[ lowest order in \((\epsilon-V)/2c^2\) ]
3 different approaches compared:

1) Wien2k (L)APW code, relativistic Dirac core, self-consistent SOC including core 2p^{1/2} radial functions (reference)

2) Wien2k (L)APW code, relativistic Dirac core, self-consistent SOC no core 2p^{1/2} radial functions in second-variational SOC step

3) FHI-aims, NAO basis set, atomic ZORA scalar relativity, non-selfconsistent SOC in second-variational step
   Advantage: Computationally affordable for hybrid functionals, large systems

Reference data set: http://dx.doi.org/10.17172/NOMAD/2017.04.27-1

High-accuracy valence and conduction DFT band structures for
50 elemental structures, 35 compound semiconductors, 21 strongly ionic compounds
69 elements included
Scalar Relativity: Close Agreement Between Accurate Methods

RMS deviation between band structures: FHI-aims (tier 2) vs. Wien2k

RMS Comparison of Spin-Orbit Coupled Band Structures

RMS deviation between band structures:
- NAOs (FHI-aims, tier 2) non-selfconsistent SOC vs. (L)APW (Wien2k) self-consistent SOC including $p^{1/2}$

Non-s.c. SOC completely accurate for valence states up to $4d$ shell ($Z=48$, Cd)

Very low errors (0.05-0.1 eV) for valence states even up to $5d$ shell ($Z=80$, Cd)

BCC Bi - Impact of Relativity

Left: Scalar relativity. Essential band structure features are wrong.


Using Numeric Atom-Centered Basis Functions: Pieces

• Numerical Integration
  \[ h_{ij} = \int d^3r \varphi_i(r) \hat{h}_{KS} \varphi_j(r) \]

• Electron density update
  \[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

• All-electron electrostatics
  \[ \nu_{es}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

• Relativity
  needed for heavy elements

• Eigenvalue solver
  \[ \frac{\hbar^2 c_k}{\epsilon_k} = \epsilon_k \frac{s}{c_k} \]

• Periodic systems
  need suitable basis, Coulomb Operator

• Coulomb operator
  \[ (ij|kl) = \int d^3r d^3r' \frac{\varphi_i(r) \varphi_j(r') \varphi_k(r) \varphi_l(r')}{|r - r'|} \]
Using Numeric Atom-Centered Basis Functions: Pieces

- **Numerical Integration**
  
  \[ h_{ij} = \int d^3r \varphi_i(r) \hat{h}_{\text{KS}} \varphi_j(r) \]

- **Electron density update**
  
  \[ n(r) = \sum_k f_k |\psi_k(r)|^2 \]

- **All-electron electrostatics**
  
  \[ v_{\text{es}}(r) = \int d^3r' \frac{n(r')}{|r - r'|} \]

- **Relativity**
  
  needed for heavy elements

- **Eigenvalue solver**
  
  \[ \frac{\hbar c_k}{\epsilon_k} = s c_k \]

- **Periodic systems**

  need suitable basis,

  **Coulomb Operator**

- **Coulomb operator**

  \[ (ij|kl) = \int d^3r d^3r' \frac{\varphi_i(r) \varphi_j(r') \varphi_k(r) \varphi_l(r')}{|r - r'|} \]

S. Levchenko
Wed 09:00h
Typical Scaling - $O(N^3)$ Wall

DFT-PBE calculations

System: Supercell models of graphene monolayer (4,050 ~ 7,200 atoms)

Basis set: 14 basis functions per atom

Problem size: 56,700 ~ 100,800

* All benchmark matrices from FHI-aims (all-electron, NAO basis)

Generic problem for any Kohn-Sham DFT code ... solution strategies?
Strategy 1: “Scale Further”

Benchmark: Alvaro Vazquez-Mayagoitia, ANL

ELPA Eigensolver: http://elpa.mpcdf.mpg.de

... but can we do better than dense eigenvalue solution when spectrum is not needed?
Strategy II: Circumvent $O(N^3)$ Bottleneck When Needed

**ELPA** (eigenvalues/vectors)
Massively parallel dense eigensolver

$O(N^3)$

Strategy II: Circumvent $O(N^3)$ Bottleneck When Needed

**ELPA** (eigenvalues/vectors)
Massively parallel dense eigensolver

$O(N^3)$

**libOMM** (density matrix)
Orbital minimization method

$O(N^3)$ with a reduced prefactor


Strategy II: Circumvent $O(N^3)$ Bottleneck When Needed

**ELPA** (eigenvalues/vectors)
Massively parallel dense eigensolver

$O(N^3)$

**libOMM** (density matrix)
Orbital minimization method

$O(N^3)$ with a reduced prefactor

---


**PEXSI** (density matrix)
Pole expansion and selected inversion exploiting sparse linear algebra

At most $O(N^2)$

## Strategy II: Circumvent $O(N^3)$ Bottleneck When Needed

<table>
<thead>
<tr>
<th>ELPA</th>
<th>(eigenvalues/vectors)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Massively parallel dense eigensolver</td>
<td></td>
</tr>
<tr>
<td>$O(N^3)$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>libOMM</th>
<th>(density matrix)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orbital minimization method</td>
<td></td>
</tr>
<tr>
<td>$O(N^3)$ with a reduced prefactor</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PEXSI</th>
<th>(density matrix)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pole expansion and selected inversion exploiting sparse linear algebra</td>
<td></td>
</tr>
<tr>
<td>At most $O(N^2)$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>And many others, including:</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScaLAPACK, $O(N)$ methods, ...</td>
</tr>
</tbody>
</table>

---


Strategy II: Circumvent $O(N^3)$ Bottleneck When Needed

**ELPA** (eigenvalues/vectors)
Massively parallel dense eigensolver

$O(N^3)$


**libOMM** (density matrix)
Orbital minimization method

$O(N^3)$ with a reduced prefactor


**PEXSI** (density matrix)
Pole expansion and selected inversion exploiting sparse linear algebra

At most $O(N^2)$


Why not switch dynamically between different solvers? Unfortunately, not easy!
- Different application programming interfaces
- Different matrix storage strategies
- Different programming languages!
Our Solution: ELSI

Open Source
Interfaces any electronic structure code with solvers
NSF-Software Infrastructure for Sustainable Innovation (SI²)

https://elsi-interchange.org

KS-DFT Codes ➔ Create Hamiltonian and overlap

Solvers
ELPA
libOMM
PEXSI
...

Compute eigenvalues, eigenvectors and density matrix

Our Solution: ELSI

Open Source
Interfaces any electronic structure code with solvers
NSF-Software Infrastructure for Sustainable Innovation (SI$^2$)

KS-DFT Codes

ELSI

Solvers

Create Hamiltonian and overlap

- Convert data format and distribution automatically

- Compute eigenvalues, eigenvectors and density matrix

**Our Solution: ELSI**

Open Source
Interfaces any electronic structure code with solvers
NSF-Software Infrastructure for Sustainable Innovation (SI²)

https://elsi-interchange.org

---

**KS-DFT Codes**

Create Hamiltonian and overlap

- Convert data format and distribution automatically
- Analyze the problem:
  - Basis set size, sparsity, property of overlap matrix, requested output, desired accuracy, available computational resource (ongoing)
  - Suggest a solver with reasonable settings (future)

**ELSI**

Matrix Conversion

**Solvers**

Compute eigenvalues, eigenvectors and density matrix

Beyond the “Cubic Wall”

Crossover: \( \sim 3,000 \) atoms
Speed-up at 7,200 atoms: \textbf{2.06x}

The Electronic Structure Library: A community-driven common library project for software development in electronic structure

One Step Further: “Electronic Structure Library” (CECAM)

eSL.cecAM.org

What does the ESL do?

Libraries

Wiki

Code repository

Data standards

Workshops

Docs

Library bundle

Library 1
Routine A

Library 2
Routine B

Code 1
Routine C

Code 2
Routine A

Routine D

Code 3
Routine E

Routine F

The ESL idea: from this...

...to this...

...to this
\[ \hat{H} \Psi = E \Psi \]
The concepts are general:

- Basis sets (Key decision upon which everything else relies!)
- Integration, density, potential update
- Seamlessly from light to heavy elements
- Excellent use of (massively) parallel hardware
- Beyond semilocal DFT for large systems