Practical Guide
to
Density Functional Theory (DFT)

Brad Malone, Sadas Shankar

Quick recap of where we left off last time

Therefore there is a direct one-to-one correspondence between the interacting ground state charge density and the external potential

Corollary: Since the integral of the charge density gives the number of electrons and determines the external potential, it determines the full Hamiltonian. Since it specifies the Hamiltonian, it also specifies the solutions of that Hamiltonian (i.e., all many-body wavefunctions, excited state.....ANY property determined by the Hamiltonian).

Kohn and Sham rewrote the HK total
energy functional as:

$$F_{HK}[\rho] = F_{KS}[\rho] = T_s[\rho] + \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}\, d^3\mathbf{r}' + E_{xc}[\rho]$$

$$= T_s[\rho] + E_{Hartree}[\rho] + E_{xc}[\rho]$$

where T_s is the kinetic energy of the particles in the non-interacting Kohn-Sham system. E_{XC} is then <u>defined</u> by this equation (thus transferring what we don't know from F_{HK} to E_{XC})

Taking the functional derivative of the KS expression with respect to either the density or the orbitals leads to the Kohn-Sham equations:

$$\left[-\frac{\hbar^2}{2m} + V_{ks}[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

where the Kohn-Sham potential is given as:

$$V_{ks}[\rho](\mathbf{r}) = V_{ext}(\mathbf{r}) + V_{Hartree}[\rho](\mathbf{r}) + V_{xc}[\rho](\mathbf{r})$$

$$V_{Hartree}[\rho](\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}'$$

$$V_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\mathbf{r})}$$

Clarification: Non-interacting particles, but INTERACTING density

$$\left[-\frac{\hbar^2}{2m} + V_{ks}[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

Rather than feel the effect of the other electrons in a direct, particle-by-particle way, Kohn Sham particles feel the presence of each other through their effect on the Kohn-Sham potential

One final, interesting point on DFT:

The Kohn-Sham approach *assumes* that the exact ground state density can be represented by the ground state of a fictitious, non-interacting system (called "non-interacting V representable").
In fact, this is not known to be true.

One final, interesting point on DFT:

The Kohn-Sham approach *assumes* that the exact ground state density can be represented by the ground state of a fictitious, non-interacting system (called "non-interacting V representable").
In fact, this is not known to be true.

Could this complicate search for better E_{xc} functionals?

BD Malone, S Shankar

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5, \mathbf{r}_6, \mathbf{r}_7, \mathbf{r}_8, \mathbf{r}_9, \mathbf{r}_{10})$$

$$\downarrow \text{DFT}$$

$$\rho(\mathbf{r})$$

BD Malone, S. Shankar

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4,\mathbf{r}_5,\mathbf{r}_6,\mathbf{r}_7,\mathbf{r}_8,\mathbf{r}_9,\mathbf{r}_{10})$$

$$\downarrow \text{DFT}$$

$$\rho(\mathbf{r})$$

...but we still have 10^{23} atoms!

Physical fact: solids can be viewed as being made up of repeating units in space

Translational invariance affects all the observable properties of a material:

$$\rho(\mathbf{r} + \mathbf{T}) = \rho(\mathbf{r})$$
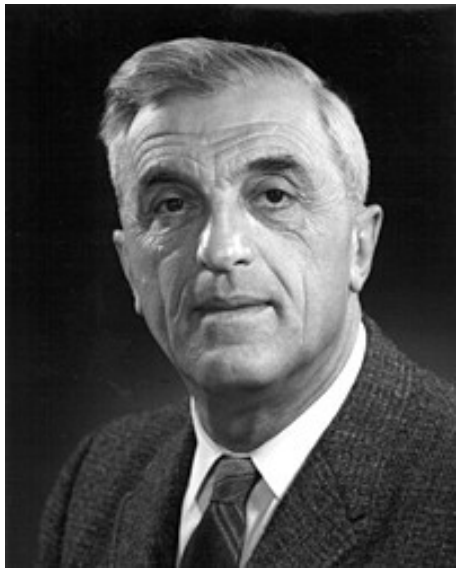$$V(\mathbf{r} + \mathbf{T}) = V(\mathbf{r})$$

etc.

Some things aren't strictly periodic in the crystal translations:

- Wavefunctions
- Collective motions of the atoms

BD Malone, S. Shankar

Some things aren't strictly periodic in the crystal translations:

- Wavefunctions
- Collective motions of the atoms

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = e^{i\mathbf{k}\cdot\mathbf{T}}\psi_{\mathbf{k}}(\mathbf{r})$$

equivalently:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$$

$$u_{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = u_{\mathbf{k}}(\mathbf{r})$$

Bloch

Not all values of k are allowed

Allowed form of the Bloch vectors:

$$\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \mathbf{b}_i$$

where m_i are integers

Not all values of k are allowed

Allowed form of the Bloch vectors:

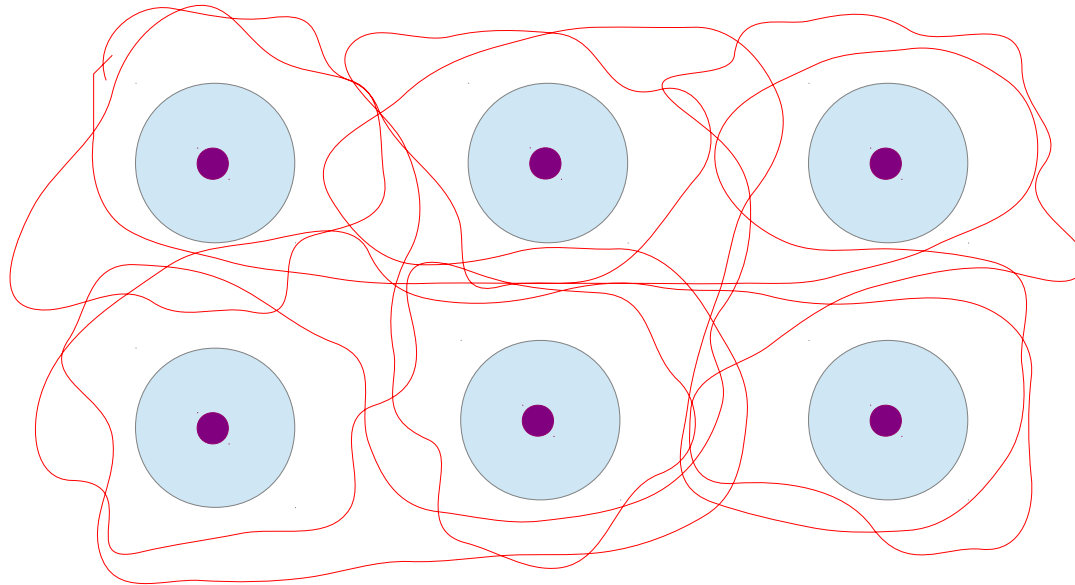$$\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i} \mathbf{b}_i$$

where m_i are integers

Brillouin zone sampling – increase the k-point sampling until convergence is reached for your desired quantity

BD Malone, S. Shankar

Taking more electrons out of the problem

Taking more electrons out of the problem

Pseudopotentials

- Pseudopotentials describe the effective interaction of the valence electrons with the ion cores.

- While DFT packages occasionally include codes to generate pseudopotentials or sometimes offer pre-made pseudopotentials for use, these need to be selected before the DFT calculation.

- The generation of pseudopotentials sometimes takes on the mystery of a 'black art', but in reality is usually pretty easy

- Pseudopotentials should always be tested prior to doing any production-level calculations.

Basis set choices

- Plane waves

- Real-space grids

- Localized functions (analytic basis functions, e.g. Gaussians as well as numerical orbitals)

- Mixed basis sets (e.g., gaussians + plane waves)

- Augmented methods (e.g., muffin-tin orbital methods)

Basis set choices

- Plane waves

- Real-space grids

- Localized functions (analytic basis functions, e.g. Gaussians as well as numerical orbitals)

- Mixed basis sets (e.g., gaussians + plane waves)

- Augmented methods (e.g., muffin-tin orbital methods)

Plane waves

Bloch form of solution:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

can be satisfied by expansion of the form:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{G}=0}^{\infty} c_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

Plane waves

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{G}=0}^{\infty} c_{\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}}$$

We can write the solution for different bands as:

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{V}} \sum_{\mathbf{G}=0}^{\infty} c_{n\mathbf{k}}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}=0}^{\infty} c_{n\mathbf{k}}(\mathbf{G}) \phi_{\mathbf{G}}(\mathbf{r})$$

Tucking in the k-point specific phase factor into the definition of the basis functions gives:

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}=0}^{\infty} c_{n\mathbf{k}}(\mathbf{G}) \phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) \qquad \phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

BD Malone, S. Shankar

Summing over infinite G vectors sounds like a complication...

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}=0}^{\infty} c_{n\mathbf{k}}(\mathbf{G})\phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) \qquad \phi_{\mathbf{G}}^{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

Coefficients decay with increasing wavevector magnitude, and thus can be truncated without loss of accuracy:

$$\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 < E_{\mathrm{cut}}$$

Plane wave energy cutoff, typically expressed in Ry (e.g., QE) or eV (e.g. VASP)

Schrodinger equation in this basis

$$\sum_{m'} = H_{m,m'}(\mathbf{k})c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k})c_{i,m}(\mathbf{k})$$

Where to make the matrix equation clearer I've altered the notation a bit from the previous slides, with the correspondence:

$$c_{i,m}(\mathbf{k}) \equiv c_{n\mathbf{k}}(\mathbf{G}_m)$$

$$H_{m,m'}(\mathbf{k}) = \frac{\hbar^2}{2m}|\mathbf{k} + \mathbf{G}_m|^2 \delta_{m,m'} + V_{eff}(\mathbf{G}_m - \mathbf{G}'_m)$$

BD Malone, S. Shankar

Fast Fourier transform (FFT)

The FFT can be used to switch from reciprocal space, to real-space, and back again, computing the terms in the Hamiltonian in the space which is most computationally efficient.

In particular, the calculation of the charge density is cheaper in real-space than it is in reciprocal space. Thus transforming the wavefunctions to real-space, (mod) squaring them to get them to get the real-space density, is preferable to straight-forwardly evaluating the expression for the charge density in reciprocal space.

DFT - seeking self-consistency

$$\left[-\frac{\hbar^2}{2m} + V_{ks}[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r})$$

Large charge redistributions occur from one iteration to the next, so a $\rho_{in}(\mathbf{r}) = \rho_{out}(\mathbf{r})$ approach will typically not converge if iterated.

The most obvious and simple strategy is simply to damp the changes by keeping more of the first input density in constructing the second input density, e.g.,

$$\rho_{in}^{n+1} = \alpha \rho_{out}^n + (1 - \alpha) \rho_{in}^n$$

Diagonalization schemes

$$\sum_{m'} = H_{m,m'}(\mathbf{k})c_{i,m'}(\mathbf{k}) = \varepsilon_i(\mathbf{k})c_{i,m}(\mathbf{k})$$

- Direct diagonalization (works well for small problems, but in plane-wave methods the dimensions of the matrix can be HUGE, making it computationally unfavorable to actually construct the full matrix.
- Iterative methods (e.g. Davidson) only require the knowledge of how the Hamiltonian acts on a particular vector. Iteratively applying an operator allows one to extract the lowest lying eigenstates (Davidson is the default in QE)
- Direct minimization of the energy functional by SD, CG (CG is a robust, secondary option in QE)

Starting a calculation: a subjective, but arguable, guide

1) Understand your structure
2) Obtain (generate or steal) pseudopotentials
3) Test your pseudopotentials on known systems (if possible)
4) Test your system for convergence in PW energy cutoff
5) Test your system for convergence in k-point sampling
6) Do project-specific calculations and associated tests

Understand your structure

• Figure out the lattice vectors and basis needed for your material. Prior papers will typically give some details. If you are given a space group and certain Wyckoff positions, the website http://www.cryst.ehu.es/cryst/get_wp.html is a great help in transforming these to actual geometric positions

• Look at your structure in a crystal viewer (e.g., XCRYSDEN) to make sure that your structure looks reasonable.
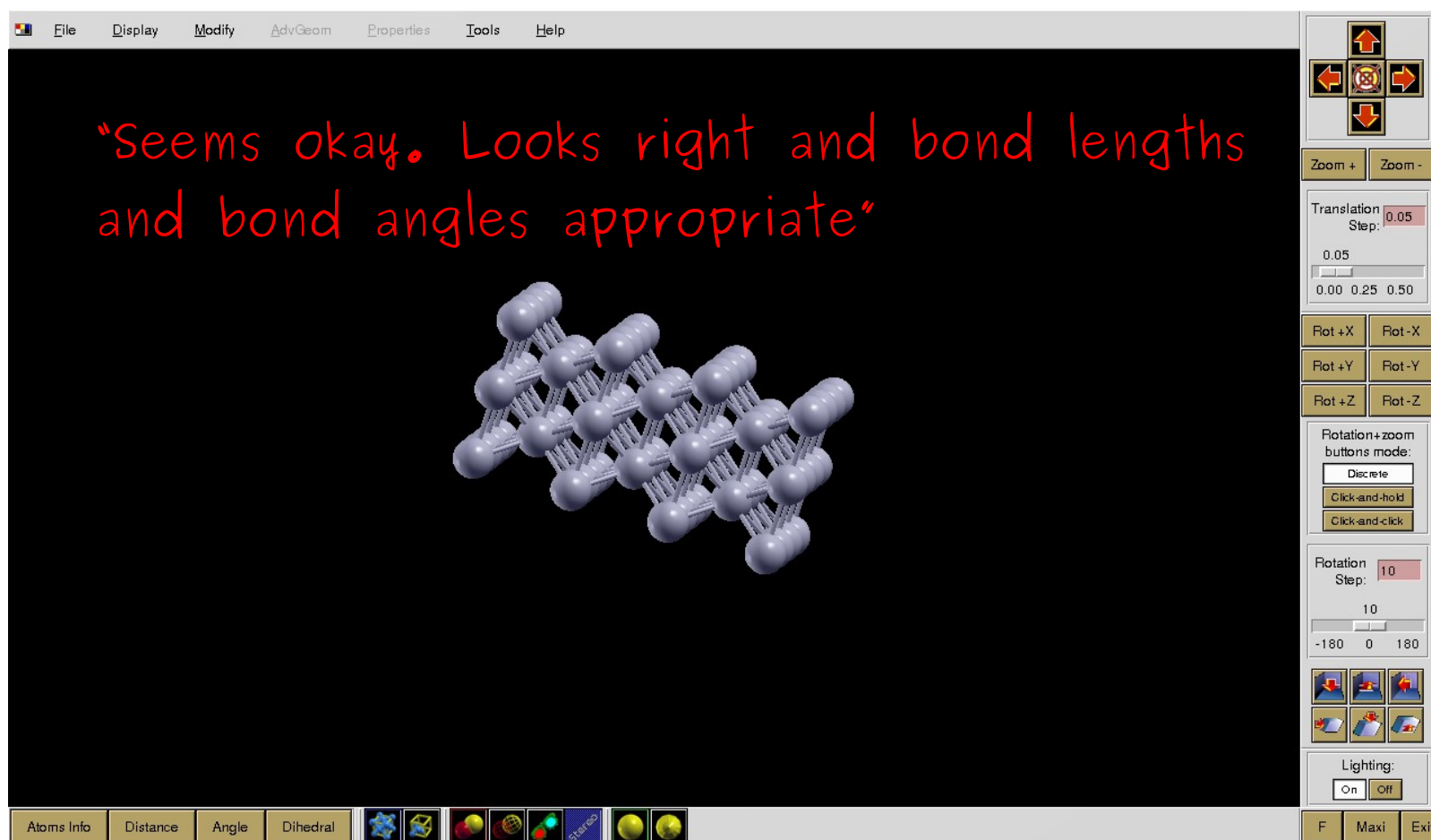
- Look at your structure in a crystal viewer (e.g., XCRYSDEN) to make sure that your structure looks reasonable.

Obtain (generate or steal) pseudopotentials

- Can obtain QE pseudopotentials (*UPF format) from the website http://www.quantum-espresso.org/pseudopotentials/

- Generate your own (QE has internal generation tools, but my personal favorite is a new code called APE (http://www.tddft.org/programs/APE/)

- Generating your own may be necessary if you have particular needs not met by those available elsewhere (e.g., small r_c for high-pressure studies, a specific partitioning between core and valence)

Test your pseudopotentials in known situations

- Can your pseudopotentials give "good" answers relative to either experiment or prior theory for known systems?

- Example: Looking to understand the vibrational frequencies of C_{60}? Can you reproduce the vibrational frequencies of diamond?

BD Malone, S. Shankar

Test plane wave cutoff for your system

- May have partially done this on testing the simpler systems in prior step

- Different properties may converge at different cutoff (e.g., total energies will often converge faster than the stress and if you relax the system, you'll care about the stress)

Test kpoint sampling for your system

- For isotropic system, kpoint sampling ratios depend inversely on unit cell dimensions

- Different properties may converge with respect to kpoint sampling differently. For example, total energies will converge much more rapidly than Raman intensities.

 BD Malone, S. Shankar

What is DFT good for?

Normally, very good for ground-state properties (remember, DFT is a theory of the ground-state)

- Cohesive energies
- Equilibrium crystal structures
- Elastic constants
- Charge densities
- Vibrational properties
- Qualitative (most of the time a pretty quantitative) prediction of band topology

What is DFT bad at?

Excited state properties:
- Band gaps [can do GW instead]
- Optical properties (electron−hole interactions) [can do BSE]

Other missing bits and trouble areas:
- Overbinding in LDA, underbinding in GGA
- Strongly correlated systems (narrow d− and f− bands)
- Lack of van der Waals interactions [can be added through the use of various schemes in addition to DFT]
- Presence of self−interaction error (electron interacts with its own charge density) [reduced by using hybrid functionals with some fraction of exact−exchange, but expensive]

Progress in improving ground state properties may lie in better exchange−correlation functionals, an active area of research