

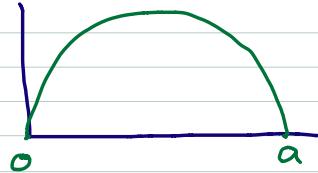
$$\text{PIAB} \quad \psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad E_n = \frac{n^2 \hbar^2}{2ma^2} \quad n=1, 2, \dots$$

$0 < x < a$

Orthonormal $\langle \psi_n | \psi_m \rangle = \delta_{nm}$

Complete set: can expand any function that is "nice" and satisfies some boundary conditions in terms of these

$$f(x) = x(a-x) \quad \text{eg}$$



$$|f(x)\rangle = \sum_n c_n |\psi_n(x)\rangle$$

$$\langle \psi_m | f(x) \rangle = \sum_n c_n \langle \psi_m | \psi_n \rangle \xrightarrow{\delta_{nm}} c_m = \langle \psi_m | f \rangle \text{ "overlap"}$$

$$|f(x)\rangle = \sum_n |\psi_n\rangle \langle \psi_n | f \rangle \neq \text{Exact if summed to } \infty$$

These ψ_n are basis functions

Maybe we don't like these boundary conditions

Slightly more general are periodic boundary conditions (PBC)

$$f(x) = f(x + Na) \quad \text{draw picture}$$

1. Hydrogen atom in a box

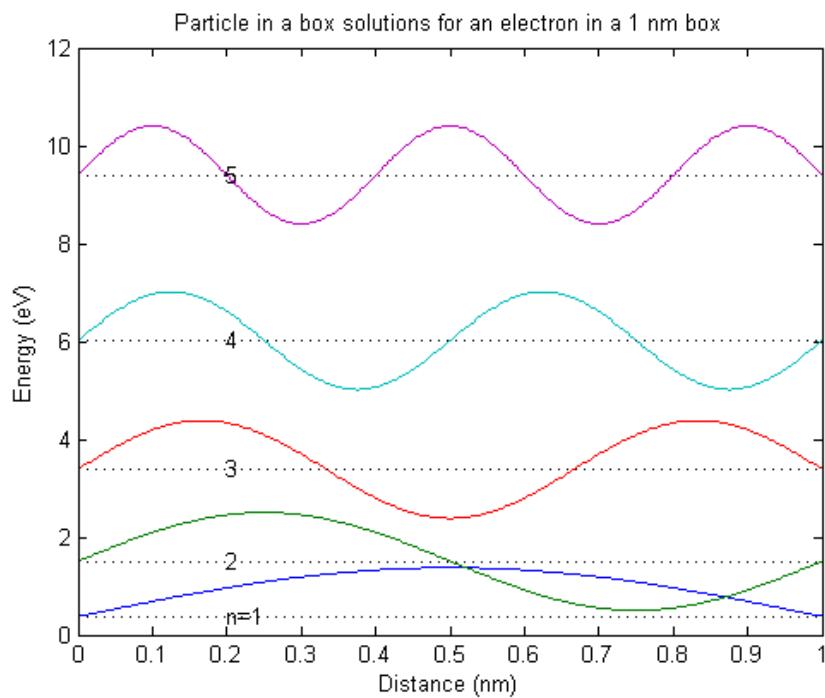
Recall H atom problem, $V(r) = -1/r$
 e^{-r} exact answer

Solved by expanding in Gaussian basis set, had to solve secular matrix containing matrix elements over basis functions

Place atom in a big box, if nucleus wasn't there, we know what the solutions look like (1-D)

$$X_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}, \quad m = 1, 2, 3, \dots$$

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2m_e a^2}$$



Could express H atom solutions as linear combinations of these. Not particularly efficient, but if it was really easy to evaluate matrix elements, might make sense to do.

It turns out to be mathematically more convenient to apply periodic boundary conditions. Keep only even n and rewrite waves as

$$X_m(x) = \frac{1}{\sqrt{a}} e^{2\pi i mx/a} = \frac{1}{\sqrt{a}} e^{iG_m x}, \quad G_m = \frac{2\pi m}{a}, \quad m = \pm 1, \pm 2, \dots,$$

$$\lambda_m = \frac{a}{|m|}, \quad E_m = \frac{\hbar^2 G_m^2}{2m_e}$$

*eigenvalues of
momentum
operator*

(Ditto y and z .) Can write solutions for H atom as linear combination of these “plane wave” basis functions:

$$\chi_i(x) = \frac{1}{\sqrt{a}} \sum_m c_{im} e^{iG_m x}, \quad G_m = \frac{2\pi m}{a}$$

If we let m run to infinity we would have a “complete” basis and could represent the H orbital exactly. In general we can’t keep an infinite number of m , so have to cut off somewhere, defined by

$$\frac{\hbar^2 G_m^2}{2m_e} < \frac{\hbar^2 G_{\text{cut}}^2}{2m_e} = E_{\text{cutoff}}$$

Defines minimum wavelength retained in basis, and thus size m of basis. Note for a given E_{cutoff} , larger a implies bigger m .

Within DFT, if we define a box size, an E_{cutoff} and a particular exchange-correlation functional, we’ve got ourselves a model!

$$\left[-\frac{1}{2} \frac{d^2}{dx^2} + v(x) + v_{\text{Coulomb}}(x) + v_{\text{xc}}[\rho(x')] \right] \psi_i(x) = \varepsilon_i \psi_i(x)$$

Kinetic energy: Diagonal in basis functions...easy!

$$\left\langle e^{iG_m x} \left| -\frac{1}{2} \frac{d^2}{dx^2} \right| e^{iG_{m'} x} \right\rangle = \frac{1}{2} (G_m)^2 \delta_{mm'}$$

Potential energy terms: Can take advantage of Fourier transforms to evaluate:

$$v(x) = \sum_m v(G_m) e^{iG_m x} \quad v(G_m) = \frac{1}{a} \int v(x) e^{-iG_m x} dx$$

$$\left\langle e^{iG_m x} \left| v(x) \right| e^{iG_{m'} x} \right\rangle = \sum_{m''} v(G_{m''}) \left\langle e^{iG_m x} \left| e^{iG_{m''} x} \right| e^{iG_{m'} x} \right\rangle = v(G_{m'-m})$$

expanded potential
in same basis
as orbitals

How many Fourier components to include in the sums? Turns out for a basis of size m you need $2m$ components to specify the potential exactly, but you can get away with smaller. The cost and accuracy of the calculation scale with this choice.

2. Periodic boundary conditions

Subtle but important point is that this approach is based on a periodic representation of a system; an artificial construction for something (like an atom or molecule) that isn’t actually periodic.

Use the term *supercell* to describe periodic box. Have to make box large enough to avoid spurious interactions between periodic images.

In particular, $v(x) + v_{Coulomb}(x)$ is periodic and long-ranged, because it contains all the electrostatic $1/r$ terms. Have to use special tricks (Ewald summations) to evaluate these sums, and have to group electrostatic terms to avoid non-convergent sums.

Key limitations of supercell approach (see *Martin*):

- Supercell must be net charge neutral (the electrostatic energy of an infinite, charged system diverges)
- Supercell must not have a net electric field
- The absolute electrostatic potential is not well-defined (there is no “vacuum” to reference an electron energy to in an infinite system).

It is possible to overcome some of these limitations by introducing compensating background charges, dipoles, multipoles, ...

3. Supercells – Cartesian and fractional coordinates

Plane-wave calculations use periodic boundary conditions. Have to define two things to describe atomic arrangement:

(1) Lattice constants of periodic cell, defined by three lattice vectors, \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3

e.g., our cube for H, but could be any of the Bravais lattices, depending on the relationships between the three vectors

Every point \mathbf{R} is equivalent to any other point $\mathbf{R}' = \mathbf{R} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$

(2) Locations of atoms within the periodic cell (the so-called “basis”)

Latter can be done by specifying locations of atoms in Cartesian coordinates \mathbf{r} .

Typically easier to specify in *fractional* coordinates \mathbf{f} of the lattice vectors.

Related by $\mathbf{r} = \mathbf{Af}$, where \mathbf{A} is matrix generated by combining lattice vectors in column form.

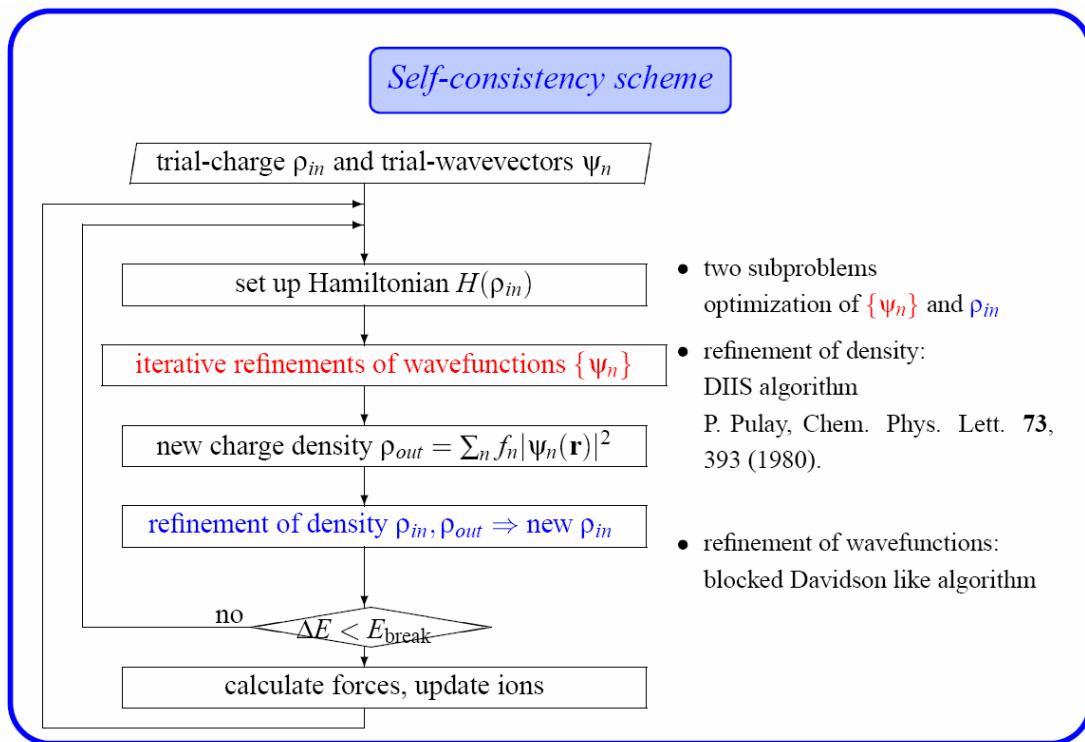
4. Gaussian v. Vasp

Compare *Gaussian* (6-311G(d,p)) and *Vasp* inputs and outputs for a spin-polarized PW91 H atom.

<i>Gaussian</i>	<i>Vasp</i>
1 input file	4 input files POSCAR: structure input INCAR: program options POTCAR: identities of atoms KPOINTS: k-point sampling (more later)
z-matrix coordinates	Atom positions relative to a supercell

Arbitrary basis set	Plane-wave cutoff
Detailed options hidden	Options “out there”
Hartree units	eV units
2 output files (.log and .chk)	<u>Lots of output files</u> OSZICAR: iteration summary OUTCAR: detailed output CONTCAR: final geometry
6 basis functions (6-311G(d,p))	9045 basis functions (!!)(10 Å cube on a side, 250 eV cutoff)
3 cycles to converge (good initial guess)	15 cycles to converge (initial plane wave guess more difficult)
Spin-up and spin-down orbital eigenvalues	Spin-component “band” energies
Total energy referenced to ionized atom	Total energy referenced to... pseudopotential atomic state

General things going on in *Vasp* calculation very similar to *Gaussian*, but details differ considerably.



5. Vasp POSCAR

POSCAR file specifies lattice vectors, numbers and types of atoms, and their positions in either Cartesian or fractional coordinates. *Vasp* uses convention in POSCAR that atoms be specified in groups of like type, and that the order in the POSCAR corresponds to the order of atoms in a composite POTCAR. Here's a POSCAR for an N2 in a 10 Å square box.

```
10 Ang. cell, diagonal orientation      ! title
10.                                     ! scale factor
1.0 0.0 0.0                            ! lattice vector a1
0.0 1.0 0.0                            ! lattice vector a2
0.0 0.0 1.0                            ! lattice vector a3
2                                         ! atom types: 2 atoms of the same type here
Cartesian                                ! positions are in (scaled) cartesians
    0. 0. 0.                             ! atom positions
0.0692820323028 0.0692820323028 0.0692820323028
```

Vasp provides a CONTCAR at the end of any job of identical format to a POSCAR, useful for restarting calculations. XDATCAR contains a trajectory in the same format.

6. Vasp INCAR input

Options to control calculation are in INCAR. Following are the ones important to calculating an energy. Options that should always be specified are underlined.

SYSTEM allows you to give some text about your calculation in the input that is echoed in the output.

NWRITE allows you to control how much is printed out.

Specify electronic state

ISPIN specifies spin polarization, 1 for off and 2 for on. Check “magmom” in your calculation for the actual number of spin up and down.

NUPDOWN specifies net number of spin-up minus spin-down electrons. Generally use only for atoms or molecules.

MAGMOM specifies the magnetic moment on each atom.

NELECT, **FERWE** and **FERDO** specifies total number of electrons and spin-up and spin-down orbital occupancies. Seldom used.

ISMEAR specifies how electrons are distributed, or “smeared out,” into the orbitals/bands near the HOMO/Fermi level. Becomes important in band calculations of bulk materials.

- 0 specifies “Gaussian” smearing, a safe option for molecules and most solids.
- 1 specifies the method of “Methfessel and Paxton,” useful in particular for relaxations in metallic systems.
- -5 specifies the “tetrahedron method with Blöchl corrections” (!), used to get reliable single point energies. Not for optimizations.
- -2 specifies set by hand, seldom used.

SIGMA sets the “smearing parameter,” which works hand-in-hand with ISMEAR. For molecules and insulators, 0.05 eV is a sensible value; for metals 0.2 eV. Large values can help convergence but too large gives unphysical results. Aim to keep the electronic “entropy” (difference between free energy and total energy) < 1 meV/atom.

Precision parameters

ENCUT specifies the plane wave energy cutoff, in eV. Vasp will select a default based on ENMAX in the POTCAR, but much wiser to specify yourself. Max(ENMAX) over all the POTCARs is a safe default. Should in general test for convergence of properties of interest with ENCUT.

PREC specifies general precision of the calculation, including things like cut-off (ENCUT), the accuracy of real-space core potential projections (LREAL), and the sizes of the FFT grids (NGX, NGY, NGZ). Use normal for normal stuff, accurate if you need high precision results.

LREAL specifies how to transform core potentials between reciprocal and real space. .FALSE. (the default) says to do it exactly, good for small cells, but more expensive. “auto” says to create optimized real-space operators. Generally more efficient.

IDIPOL turns on “dipole corrections” to the total energy. Important only in calculations in which the supercell has a large dipole moment.

LORBIT is not a precision parameter, but it turns on printing out of charge analyses. -11 is a good default value.

Self-consistent field parameters

ALGO specifies the SCF algorithm. Note *Vasp* separates the problem into optimizations of the wavefunction and the charge density. At the end of the SCF the two are consistent, but during the course of the SCF they are not. The default ALGO=fast uses a sequence of block diagonalization and DIIS methods that are, well, fast. ALGO=normal uses the safer but slower diagonalization method alone. In general SCF is more touchy for periodic systems. Never bother to calculate all orbitals (termed “bands”), only occupied and a few unoccupied.

NBANDS specifies how many bands (orbitals) to calculate. You always want to calculate all the occupied ones and, for numerical reasons, at least some of the unoccupied ones. In general for performance reasons you don’t need or want to calculate all of the empty ones. The default is safe.

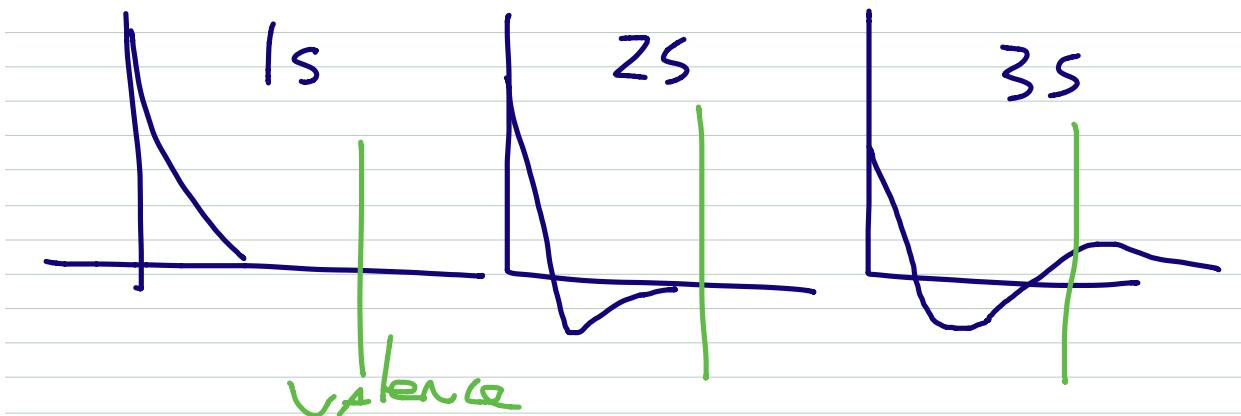
EDIFF specifies the SCF convergence criterion. 1e-4 for routine, 1e-5 for more accurate.

NELM specifies maximum number of SCF cycles. If your calculation does not converge after the default number of steps, DO NOT just increase NELM!!!! Look carefully at change in energy, at the orbital occupancies, all the other computational details. Lack of convergence is telling you something!

Problem - core wavefunctions have high KE / short λ
 would require very high cutoff to describe

$$\psi_{1s} \sim e^{-Zr/a_0} \quad \text{would be nice to demonstrate finite expansion of this}$$

Valence wavefunctions vary slowly in region that bonding occurs, but vary rapidly near core to orthogonalize w/ valence



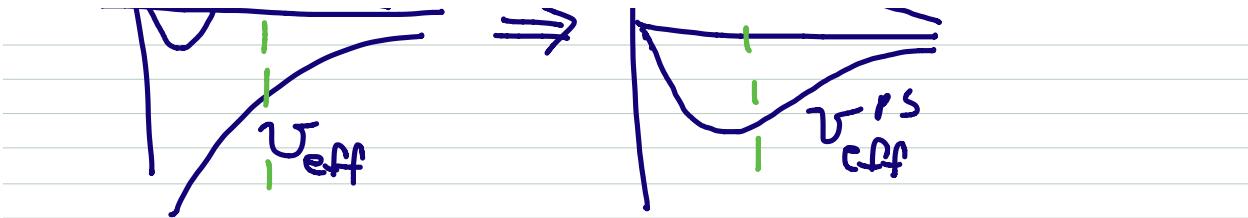
Idea - remove core region from problem

Create effective "potential" that accounts for effect of core on valence

$$\begin{array}{l} \text{valence} \left\{ \begin{array}{ll} 3p & = \\ 3s & = \end{array} \right. \qquad \begin{array}{ll} 3p & = \\ 3s & = \end{array} \\ \text{core} \left\{ \begin{array}{ll} 2p & = \\ 2s & = \\ 1s & = \end{array} \right. \Rightarrow \end{array}$$

$$\left\{ -\frac{1}{2}\nabla^2 + V_{\text{eff}}[\rho] \right\} \psi = E \psi \quad \left\{ -\frac{1}{2}\nabla^2 + V_{\text{eff}}^{ps}[\rho] \right\} \psi^{ps} = E \psi^{ps}$$





Goal - keep energies the same, keep valence region the same
within electron-electron interactions

These pseudopotentials must be created somehow

Describe terminology

Orthogonalized plane wave (OPW) idea

Say we know $1s, 2s$ states. Finding difference between $3s$ + these is just as good as finding $3s$ itself.

Create basis functions that have core functions subtracted off

$$X_G(x) = e^{iGx} \Rightarrow X_G(x) = \phi_m(x) + \sum_m b_{mg} \underbrace{\phi_m(x)}_{\text{OPW basis}} \quad b_{mg} = \langle \phi_m | e^{iGx} \rangle \quad \text{atom-centred fns}$$

X_G not orthonormal

Could write in projector form $X_G = \hat{T} X_G$

$$\hat{T} = 1 + \sum_m |\phi_m(x)\rangle \langle \phi_m(x)|$$

Solve Schrödinger eq in OPW basis

$$\psi = \sum_G c_G X_G$$

solve generalized secular equation for c_G

$$HC = SCE$$

have to evaluate $\langle X_G | \hat{h} | X_G \rangle \rightarrow$

... if OPW ...

$$\langle \chi_G | h^{---} | \chi_{G'} \rangle$$

$$V_{\text{eff}}^{\text{OPW}} = V_{\text{ext}} + \sum_m (\epsilon - \epsilon_m) |\phi_m\rangle \langle \phi_m|$$

smoother, more complicated

But... complicated part can be replaced with simpler approx forms.

Three choices:

- OPW use this exactly, with atomic core orbitals
- approximate potential somehow to retain valence properties - PR
- partition into core spherical region and smoother valence region - PAW

ISTART, INIWAV, ICHARG specify how to initialize the wavefunction and charge density.

Exchange-correlation parameters

GGA specifies the DFT functional. The POTCARs are constructed for specific GGAs, and by default the exchange-correlation functional is determined from the POTCARs.

LASPH determines how the exchange-correlation functional is evaluated in the core regions of atoms. Default is .FALSE., to evaluate using a spherical approximation. .TRUE. includes non-spherical contributions and should be used for magnetic centers, e.g. in oxides (Mike!).

LHFCALC provides access to Hartree-Fock and “hybrid” functionals. This is very new and very expensive, so use only after careful study of the literature!

7. Core electron treatments

What is hiding in the POTCAR? A description of the atomic (frozen) cores!

Plane waves are poor choice for treating wavefunctions near atomic cores:

Rapid oscillations → high kinetic energy → “high m ” plane waves

One approach is to “augment” the plane waves (APW) with functions that better represent the atomic character of orbitals in spherical regions around the atoms. In general, quite expensive approach. Modern “linearized augmented plane wave” (LAPW) approach makes it tractable, still not in broad use.

Alternative is to replace explicit treatment of cores with implicit treatment that captures the effects of the atomic cores on the valence orbitals.

Relativity

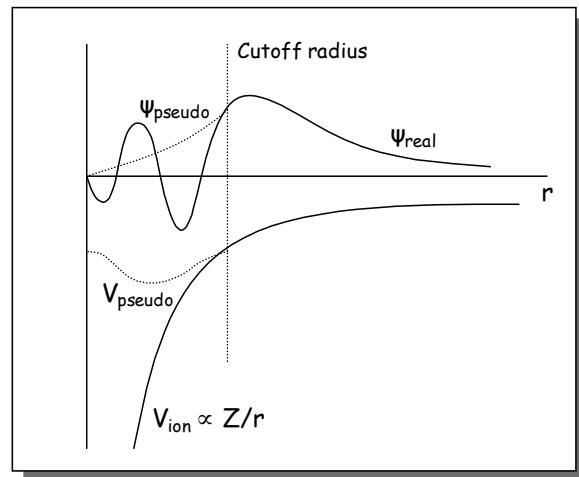
Relativistic effects are greatest in the core regions (mass-velocity, Darwin, spin-orbit). All the following approaches allow the relativistic effects to be treated for the core states, so that the indirect effects propagate into the valence.

Pseudopotential models

Idea is to replace core electrons and their effect on the valence electrons with a “pseudopotential.” Establish radial cutoff between core and valence regions, choose specific atomic configurations, construct PP to go smoothly into real potential outside of cutoff radius.

Preserves phase and shape of valence wavefunctions outside cutoff, but loose this detail in the core region.

Standard jargon:



Transferability – ability of PP to be applied in different chemical environments

Local vs. non-local – Spherically symmetric (local) vs. l -dependent (non-local)

Norm-conserving – Preserving $|\psi|^2$ of valence wavefunctions; important for getting long-range Coulomb potential correct

Soft vs. hard –

Hard: closer to true atomic potential, requiring large KE cutoff

Soft: larger perturbation on atomic potential, allowing smaller KE cutoff

Ultra-soft (Vanderbilt) pseudo-potential: relax norm-conservation constraint to reduce cutoff, and compensate by putting “augmentation” charges on all atoms. These were the first potentials to enable efficient large-scale calculations.

Projector augmented wave (PAW)

PAW most modern approach, combines advantages of APW and of ultrasoft PPs. Not strictly a PP approach: constructs full wavefunction as combination of valence (plane wave) part and precomputed core parts from atomic calculations using same XC potential. Retains full nodal structure of valence wavefunctions.

Generation of these potentials is not for the casual user (just as the case for making AO basis sets). The great strength of *Vasp* is a very complete and reliable library of potentials for the whole periodic table and for several exchange-correlation functional.

Following slides borrowed from Georg Kresse presentation:

Pseudopotential approximation

- the number of plane waves would exceed any practical limits except for H and Li
 - ⇒ pseudopotentials instead of exact potentials must be applied
 - three different types of potentials are supported by VASP
 - norm-conserving pseudopotentials
 - ultra-soft pseudopotentials
 - PAW potentials
 - they will be discussed in more details in later sessions
 - all three methods have in common that they are presently **frozen core** methods
 - i.e. the core electrons are pre-calculated in an atomic environment and kept frozen in the course of the remaining calculations

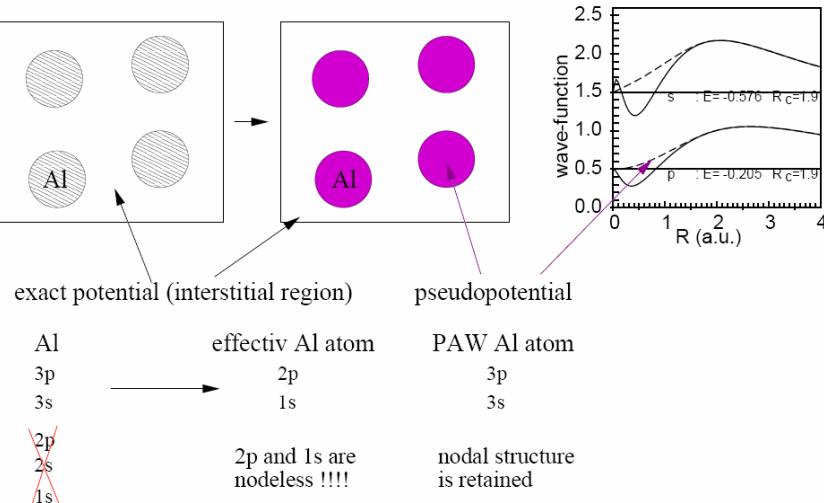
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G. KRESSE, PSEUDOPOTENTIALS (PART I)

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Pseudopotential: essential idea

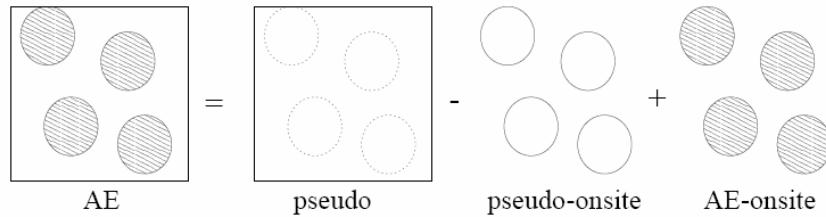


G. KRESSE: PSEUDOPOTENTIALS (PART I)

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PAW: addidative augmentation

- character of wavefunction: $c_{lme} = \langle \tilde{p}_{lme} | \tilde{\Psi}_n \rangle$
 - $|\Psi_n\rangle = |\tilde{\Psi}_n\rangle - \sum |\tilde{\phi}_{lme}\rangle c_{lme} + \sum |\phi_{lme}\rangle c_{lme}$



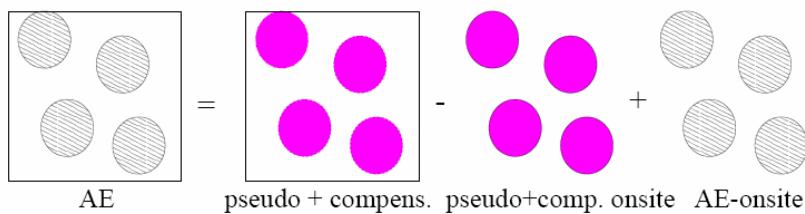
- same trick works for ρ_{H}
 - wavefunctions
 - charge density
 - kinetic energy
 - exchange correlation energy
 - Hartree energy

G. KRESSE, PSEUDOPOTENTIALS (PART II) AND PAW

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Hartree energy

- the pseudo-wavefunctions do **not have the same norm** as the AE wavefunctions inside the spheres
 - to deal with long range electrostatic interactions between spheres
a soft compensation charge \hat{n} is introd. (similar to FLAPW)



- Hartree energy becomes: $E_H = \tilde{E} - \tilde{E}^1 + E^1$

$$E_H[\tilde{n} + \hat{n}] - \sum_{\text{sites}} E_H[\tilde{n}^1 + \hat{n}^1] + \sum_{\text{sites}} E_H[n^1 + \hat{n}^1]$$

\hat{n}^1 pseudo-charge at one site \hat{n}^1 compensation charge at site

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PAW energy functional

P.E. Blöchl, Phys. Rev. B**50**, 17953 (1994).

- total energy becomes a sum of three terms $E = \tilde{E} + E^1 - \tilde{E}^1$

$$\begin{aligned}\tilde{E} &= \sum_n f_n \langle \tilde{\Psi}_n | -\frac{1}{2} \Delta |\tilde{\Psi}_n\rangle + E_{xc}[\tilde{n} + \hat{n} + \tilde{n}_c] + \\ &\quad E_H[\tilde{n} + \hat{n}] + \int v_H[\tilde{n}_{Zc}] (\tilde{n}(\mathbf{r}) + \hat{n}(\mathbf{r})) d^3\mathbf{r} + U(\mathbf{R}, Z_{\text{ion}}) \\ \tilde{E}^1 &= \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \tilde{\phi}_i | -\frac{1}{2} \Delta |\tilde{\phi}_j\rangle + \overline{E_{xc}[\tilde{n}^1 + \hat{n} + \tilde{n}_c]} + \right. \\ &\quad \left. \overline{E_H[\tilde{n}^1 + \hat{n}]} + \int_{\Omega_r} v_H[\tilde{n}_{Zc}] (\tilde{n}^1(\mathbf{r}) + \hat{n}(\mathbf{r})) d^3\mathbf{r} \right\} \\ E^1 &= \sum_{\text{sites}} \left\{ \sum_{(i,j)} \rho_{ij} \langle \phi_i | -\frac{1}{2} \Delta |\phi_j\rangle + \overline{E_{xc}[n^1 + n_c]} + \right. \\ &\quad \left. \overline{E_H[n^1]} + \int_{\Omega_r} v_H[n_{Zc}] n^1(\mathbf{r}) d^3\mathbf{r} \right\}\end{aligned}$$

G. KRESSE, PSEUDOPOTENTIALS (PART II) AND PAW

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- \tilde{E} is evaluated on a regular grid

Kohn Sham functional evaluated in a plane wave basis set

with additional compensation charges to account for the incorrect norm of the pseudo-wavefunction (very similar to ultrasoft pseudopotentials)

$$\hat{n} = \sum_n f_n \tilde{\Psi}_n \tilde{\Psi}_n^* \quad \text{pseudo charge density}$$

$$\hat{n} \quad \text{compensation charge}$$

- E^1 and \tilde{E}^1 are evaluated on radial grids centered around each ion

Kohn-Sham energy evaluated for basis sets $\{\tilde{\Psi}_i\}$ and $\{\Psi_i\}$

these terms correct for the shape difference between the pseudo and AE wavefunctions

- no cross-terms between plane wave part and radial grids exist

G. KRESSE, PSEUDOPOTENTIALS (PART II) AND PAW

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US-PP or PAW potentials

the general rule is to use PAW potentials wherever possible

- less parameters involved in the construction of PAW potentials
 - improved accuracy for:
 - * magnetic materials
 - * alkali and alkali earth elements, early 3d elements to left of periodic table
 - * lanthanides and actinides
 - generation of datasets is fairly simple (certainly easier than for US-PP)
 - general construction scheme is similar for US-PP and PAW potentials
- most of the PAW potentials were generated 5 years after the US-PP
a different philosophy

G. KRESSE, THE PAW AND US-PP DATABASE
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Pseudopotentials – NC, USPP, PAW

PAW versus US-PP potentials

- the PAW potentials are generally of similar hardness across the periodic table
- most of the PAW potentials were optimised to work at a cutoff of 250-300 eV
- PAW potentials are usually slightly harder than US-PP
- for compounds where often species with very different covalent radii are mixed, the PAW potentials are clearly superior
- for one component systems the US-PP might be slightly faster (at the price of a somewhat reduced precision)
- for the US-PP the radial cutoff were chose according to the covalent radius (periodic table)
- the US-PP become progressively softer when you move down in the periodic table

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The PAW potentials

three different flavours, one LDA (CA) and two GGA's (PW91 and PBE)

- download location of LDA potentials: [paw/potcar.date.tar](#)
- download location of PW91 potentials: [paw_GGA/potcar.date.tar](#)
- download location of PBE potentials: [paw_PBE/potcar.date.tar](#)
- I recommend to use either the **LDA** or the **PBE** potentials
the PBE implementation follows strictly the PBE prescription, whereas the PW91 description is not that strict
(for the LDA part, the parametrisation of Perdew and Zunger is used, instead of Perdew's Pade approximation)
for the PBE potentials, you do not need to specify VOSKOWN=1 in the INCAR file, since this is the default

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Standard PAW potentials and Energy Cutoffs

B_h	700	C_h	700	N_h	700	O_h	700	F_h	700
B	318	C	400	N	400	O	400	F	400
B_s	250	C_s	273	N_s	250	O_s	250	F_s	250
Al	240	Si	245	P	270	S	280	Cl	280
Al_h	295	Si_h	380	P_h	390	S_h	402	Cl_h	409
Ga	134	Ge	173	As	208	Se	211	Br	216
Ga_d	282	Ge_d	287						
Ga_h	404	Ge_h	410						
In	95	Sn	103	Sb	172	Te	174	I	175
In_d	239	Sn_d	241						
Tl	90	Pb	98	Bi	105				
Tl_d	237	Pb_d	237	Bi_d	242				

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	PAW	hard	AE
H ₂	1.447		1.446 ^a
Li ₂	5.120		5.120 ^a
Be ₂	4.520		4.521 ^a
Na ₂	5.663		5.67 ^a
CO	2.141	2.128	2.129 ^a
N ₂	2.076	2.068	2.068 ^a
F ₂	2.633	2.621	2.615 ^a
P ₂	3.570		3.572 ^a
H ₂ O	1.839	1.835	1.833 ^a
$\alpha(\text{H}_2\text{O})^{\circ}$	105.3	104.8	105.0 ^a
BF ₃	2.476	2.470	2.464 ^b
SiF ₄	2.953	2.948	2.949 ^b

^a NUMOL, R.M. Dickson, A.D. Becke, J. Chem. Phys. **99**, 3898 (1993).

^b GAUSSIAN94, S. Goedecker, et al., Phys. Rev. B **54**, 1703 (1996).

- results for the bond length of several molecules obtained with the PAW and AE approaches
- using standard PAW potentials (and hard PAW potentials)
- well converged relaxed core AE calculations yield identical results

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The energy zero

- in VASP all energies are referred to the the reference state for which the potential was generated!
this is in most cases not the real groundstate of the atom
- to determined the energy of the grounstate of the atom place the atom in a larger non cubic box to break initial symmetry (i.e. 11 Å × 10 Å × 9 Å)
use the Γ point only

INCAR:

```
ISPIN = 2           ! spin polarized
ISMEAR = 0 ; SIGMA = 0.2 ! for small sigma conv. for TM is diff.
MAGMOM = 2          ! initial magnetic moment
```

one should use the energy value energy without entropy of the OUTCAR file since this converges most rapidly to the correct energy for sigma→0

- $E_{\text{coh}} = E_{\text{metal/molecule}} - nE_{\text{atom}}$

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8. Comparing energies between calculations

When comparing energies between different calculations, e.g. to calculate reaction energies, must make sure to use the same cutoff, potentials, and all other key parameters underlined in section 5 in all calculations! Look for the “total energy” in the output.

9. Wavefunctions and charge densities

As with any electronic structure calculation, the primary outputs are the total energy, the charge density, and the orbitals (or “bands”). Vasp provides some tools to look at these:

Setting **LCHARG**=.TRUE. turns on creation of the CHGCAR, which contains the total charge density (and, for spin-polarized calculations, the spin-up minus spin-down density) evaluated on the $\text{NGX} \times \text{NGY} \times \text{NGZ}$ grid. Not so interesting by itself, but by calculating a system and its parts identically in the same supercell, charge-density-differences can be created that show how charge “moves” when bonds are made.

Setting **LWAVE**=.TRUE. turns on output of a WAVECAR, which includes everything about the final wavefunctions. Used primarily to restart calculations.

LORBIT controls output of the DOSCAR and PROCAR which contain analysis of the total density of states and of each band, respectively. Controlled with RWIGS, EMIN, and EMAX.

A supplementary code exists to extract Bader charges from the CHGCAR.

10. Exploring potential energy space

Forces calculated using Hellman-Feynman theorem. No concern about Pulay forces (derivatives of basis functions wrt atom positions).

Generally limited to Cartesian coordinates in supercell calculations—no internal coordinates, redundant coordinates. As with everything else, these can be more ill-behaved than *Gaussian* optimizations.

There is an option in the POSCAR file to allow motions of only some of the atoms, called Selective Dynamics. Primarily useful when modeling surfaces.

Geometry optimizations

IBRION = 2 turns on a conjugate-gradient optimization, safe but slower.

IBRION = 1 turns on a quasi-Newton-Raphson, DIIS optimization. Uses a diagonal Hessian guess that gets updates. Great close to minima or TS, hazardous otherwise. **NFREE** specifies how many previous steps to keep in the DIIS algorithm. Should always be less than the total number of degrees of freedom, and probably no bigger than 10.

IBRION = 3 turns on damped molecular dynamics, evidently good when you really have a bad initial guess. I’ve never tried it.

NSW sets the maximum number of geometry steps. 0 means a single-point calculation, > 0 means an optimization.

EDIFFG determines the convergence criterion. > 0 means the optimization stops when the difference in energy between two steps is $< \text{EDIFFG}$. < 0 means the optimization stops when the maximum force is $< |\text{EDIFFG}| \text{ eV}/\text{\AA}$. I prefer the latter. -0.05 is good for normal stuff, -0.03 for

publication quality, might need even smaller if you want to calculate accurate frequencies. Note that the smaller EDIFFG is, the smaller EDIFF should be.

POTIM scales the forces that are used in the optimization. The efficiency of optimizations can be sensitive to this. Start with the default 0.5, and if you are going to be doing a lot of calculations look at the manual for how to set more reliably.

ISW specifies whether to vary the atoms, the lattice vectors, or both. ISW = 1 just moves the atoms, which is usually what you want.

Frequency calculations

IBRION = 5 turns on a “dumb” numerical Hessian and frequency calculation that moves every atom NFREE steps in the x, y, and z directions. NFREE = 2 gives 2-sided differences. POTIM specifies the step size, probably 0.01 or 0.015 Å.

IBRION = 6 turns on a smarter algorithm that takes advantage of any symmetry to cut down on the number of force evaluations needed.

IBRION = 7 and 8 turns on an analytical, perturbation-theory-based evaluation of the Hessian matrix. Never tried it.

Molecular dynamics

IBRION = 0 turns on molecular dynamics, when you just want to shake things up! MD is *expensive*, so you will want to scale back on all your precision parameters, like PREC = low and a lower ENCUT. Better turn symmetry off (ISYM = 0).

NSW sets the number of MD steps, and **POTIM** the timestep in fs.

SMASS = -3 turns on a simple NVE MD run; energy is conserved (or ought to be).

SMASS = -1 turns on a scaled velocity MD. This allows you to do a simulated annealing, starting from a high temperature and gradually cooling, or to roughly simulate a fixed temperature. NBLOCK controls the frequency with which the velocities are rescaled.

SMASS > 0 turns on an NVT MD run, and the value of SMASS specifies the thermostat mass. Ask an expert.

TEBEG, **TEEND** specify the initial and final temperatures in the MD run. Initial velocities are set randomly according to TEBEG.