Basis Sets & Pseudopotentials

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Basis Sets

- To solve in practice one has to use a finite Hilbert space

- goals:

  - efficency

  - accuracy

LCAO

- Single atoms can be solved efficiently

- Molecules distort the atoms: orbitals of the unperturbed atom might be used as basis

- Linear Combination of Atomic Orbitals

- works reasonably well, needs only a small number of orbitals

- reference basis 6-31++G(3df,3pd) has 18 AO for H (1 e) and 39 for C (6 e) and 47 for Mg (12 e)

- selection of "natural" orbitals

H-like

- H like atoms (single electron) can be solved exactly

$$Q_{nl}(Zr)exp(-\frac{Zr}{n})Y_l^m(\theta, \phi)$$

- effective charge Z

- can be used and and works well, but is cumbersome

STO

- simplify H like by setting

$$Q_{nl}(Zr) = r^l$$

- can be accurate

- simpler, but still computational expensive

Polarization

- first response of atom is probably how it gets deformed when it is in a molecule

- important to describe many effects

- normally use AOs for occupied orbitals (+ maybe some) and add polarization

Molecularly optimized

- Same approach as polarization, but looking at the perturbation on the atom made by other atoms (in molecules)

- condition number of overlap matrix is also optimized

- Joost VandeVondele & Juerg Hutter

Gaussian orbitals (GTO)

$$r^l Y_{lm}(\theta, \phi) exp(-\alpha r^2)$$

~ can be efficiently evaluated: most contributions have simple analytic expression

~ product of gaussians -> gaussian

~ decomposes in x,y,z directions

$$exp(-\alpha r^2) = exp(-\alpha x^2) exp(-\alpha y^2) exp(-\alpha z^2)$$

- "wrong" asymptotic -> use several of them

- Linear combination of gaussians

- approximate AOs, STOs, polarization using them

Augmentation

- use diffuse functions to recover the correct asymptotic

- important to reduce the error in gas phase

Numerical AO

- use a finite radial grid to represent AOs

- difficult to get the electrostatic

- normally not as efficient as gaussians

- finite support

Non Orthogonality

- all previous basis set are atom centered

- non orthogonal between atoms

- overlap $\quad S_{\mu\nu} = \int \psi_\mu \psi_\nu$

BSSE

- Several problems due to this

  - general eigenvalue problem

  - basis depends on atom position

  - approximation is not constant -> BSSE

  - gas phase, surfaces, condensed phase less

Plane Waves

- orthogonal

- uniform $exp(i < k, r >)$

  - can be efficiently handled

- core electrons difficult to represent

- describe empty space

Mixed Basis Sets

- separate space into regions
- Muffin Tin Approximation
  - close to atom AOS
  - slowly varying outside

APW

- plane waves for the interstitial region
- GTO for the core region
- KKR spherical waves outside (multiple scattering)

- whole density in gaussians

- put a smooth part on plane waves

- residual density mostly atom centered

- atomic expansion of it

- expand also smooth density in gaussians

~ split the density in a smooth part and a

RI methods

- expand the density in single gaussian basis to reduce coulomb term calculation

Pseudo potentials

- active electrons

- try to describe only the valence electrons

- first approximation: frozen core

$$\psi_v = \phi_v + \sum \alpha_{cv} \psi_c$$

- ϕ_v smooth

$$[H + \sum_c (\epsilon_v - \epsilon_c)\psi_c\psi_c^*]\phi_v = \epsilon_v\phi_v$$

- non normalized ϕ_v

- arbitrary projector

Norm conservation

- scattering approach: reproduce correct

$$< q|V|q' >$$

- logarithmic derivative defines it

$$-\frac{1}{2\psi^2(r)} \int_0^r |\psi(t)|^2$$

Calculating a pseudo

- all electron calculation for a reference state

- for each l choose a cutoff radius r_c^l

- ϕ ground state -> nodeless

- invert the Schrödinger equation and get the screened pseudopotential

- unscreening (get the ionic potential)

~ **centrifugal barrier for** $l > l_{max}$ **taken from a reference l**

Semilocal and Separable

- The non local part V is approximated as

$$V = \sum_{l,m} \frac{|V_l|Y_{l,m}><Y_{l,m}|V_l|}{<Y_{l,m}|\delta V_l|Y_{l,m}>}$$

- sum of projectors

$$V = \sum_{l,m} p^*_{l,m} e_{l,m} p_{l,m}$$

- matrix element between plane waves is a product

- simple, and has computational advantages

- might introduce "ghost states" (solution with nodes an lower energy)

- there conditions and recipes to avoid that

Ultrasoft

- difficult to improve 1s,2p,3d,... where no nuclear repulsion is present

- Vanderbilt

  - remove norm conservation, but introduce more reference states to improve transferability

NLCC

- xc energy is not linear, so contribution of pseudopotential do not cancel perfectly out

- add a core density to the density on which the xc potential is calculated

- can smooth the cusp at the core, something that makes xc evaluation difficult

Relativistic corrections

- in the solution of the atomic problem used for the pseudopotential calculation one can easily use scalar relativistic calculations

- as core electrons are the ones that need most correction this is a good way to keep them into account

- needed for heavy elements

Advantages

- less electrons (cheaper)

- relativistic correction

- reduced BSSE