

Using pseudopotentials

Peter Reinhardt

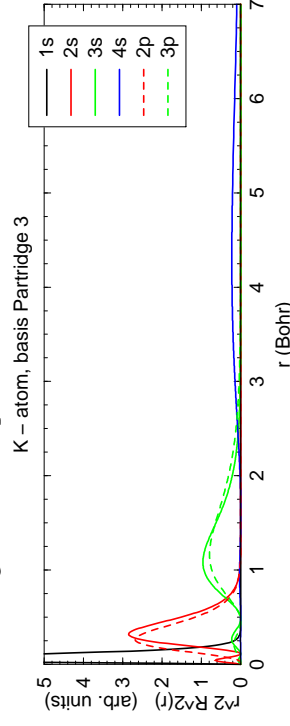
Laboratoire de Chimie Théorique, Université Paris VI, 75252 Paris CEDEX 05,
Peter.Reinhardt@upmc.fr

-p.14

-p.34

Motivation

- Calculations scale with $N^3 \dots N^8$
- N being the number of basis functions \sim number of electrons.
- Chemistry deals with the valence electrons only
 - Frozen core approximation
 - Different regions in real space



- Exclude core electrons completely from the calculations
 - Model potentials
 - Pseudopotentials

-p.24

-p.44

Frozen core approximation

Ingredients for a correlation calculation

- Fock matrix in molecular orbitals

$$F_{ij} = h_{ij} + \sum_{k \in \text{occ}} 2(ij|kk) - (ik|kj)$$

- Monoelectronic integrals
- Bielectronic integrals
- Orbital energies = diagonal elements of F :

$$h_{ij} \\ (ij|kl)$$

$$\begin{aligned} \epsilon_i &= F_{ii} = h_{ii} + \sum_{k \in \text{occ}} 2(ii|kk) - (ik|ki) \\ &= h_{ii} + \sum_{k \in \text{occ}} 2J_{ik} - K_{ik} \end{aligned}$$

- Hartree-Fock energy

$$E_{\text{HF}} = E_N + \sum_{i \in \text{occ}} h_{ii} + \epsilon_i$$

Frozen core approximation

Leave only valence indices in the calculations

- Modified nuclear energy

$$E'_N = E_N + 2 \sum_{i \in \text{core}} h_{ii} + \sum_{i,j \in \text{core}} 2(ii|jj) - (ij|ji)$$

- Modified one-electron integrals

$$h'_{ij} = h_{ij} + \sum_{k \in \text{core}} 2(ij|kk) - (ik|kj)$$

- Same Fock matrix elements

$$F'_{ij} = h'_{ij} + \sum_{k \in \text{valence}} 2(ij|kk) - (ik|kj) = F_{ij}$$

- Keep only bielectronic integrals with 4 valence/virtual indices

Frozen core approximation

- Leaves Hartree-Fock energy unchanged

$$E_{\text{HF}} = E'_N + \sum_{i \in \text{valence}} h'_{ii} + \epsilon'_i$$

- Changes decomposition into nuclear, one-electron and two-electron contributions:

```

ENERGIES AFTER ORBITAL FREEZING
RECALCULATED ONE-ELECTRON ENERGY:  -41.5486119416524
RECALCULATED TOTAL ENERGY          -76.0601469630512
RECALCULATED ONE-ELECTRON ENERGY  -41.5486119416524
RECALCULATED TWO-ELECTRON ENERGY   17.6100077216435
EFFECTIVE NUCLEAR REPULSION         -52.1215427430423
READ TOTAL ENERGY                  -76.0601469636000
READ ONE-ELECTRON ENERGY          -123.055776340000
READ TWO-ELECTRON ENERGY           37.7986949980000
READ NUCLEAR ENERGY                9.19693437840000

DIFFERENCES
TOTAL :  5.487947873916710E-010
    
```

-p.86

-p.86

Frozen core approximation

- Allows to use same formulae as before for correlation, like

$$E_{\text{MP}}^{(2)} = \sum_{ij \in \text{valence}} \sum_{ab \in \text{virtual}} \frac{[2(i a | j b) - (i b | j a)](i a | j b)}{F_{ii} + F_{jj} - F_{aa} - F_{bb}}$$

- Repartition into H_0 and V different:

| H ₂ O | all-electron | 1s frozen |
|------------------|--------------|-----------|
| HF | -76.0601 | -76.0601 |
| E_N | 9.1969 | -52.1215 |
| MP0 | -38.2615 | -58.4501 |
| MP1 | -37.7987 | -17.6100 |
| MP2 | -0.2580 | -0.2342 |
| MP3 | -0.0027 | -0.0023 |
| total | -76.3208 | -76.2966 |
| CPU time | 15.0 sec | 8.0 sec |

-p.86

-p.106

Drawback

- Initial Hartree-Fock calculation with all orbitals
- Get initial core orbitals from atomic calculations
- Orthogonalize these core orbitals (and all others after that)
- Freeze the core orbitals via

$$F = \begin{pmatrix} \epsilon_1 & 0 & 0 & 0 & \dots & 0 \\ 0 & \epsilon_2 & 0 & \vdots & \ddots & \vdots \\ 0 & 0 & \epsilon_3 & 0 & \dots & 0 \\ 0 & \dots & 0 & \epsilon_4 & \dots & F_{4n} \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & \dots & 0 & F_{n4} & \dots & \epsilon_n \end{pmatrix}$$

Diagonalization does not change the first 3 orbitals

- Need all molecular orbitals and the 4-index transformation ?
No, construct h'_{ij} and E'_N before the transformation

Projection

J.C.Phillips, L. Kleinman, Phys.Rev., 116 (1959) 287

Write the Fock operator through a spectral representation

$$\hat{F} = \sum_{i \in core} \epsilon_i |\phi_i\rangle \langle \phi_i| + \sum_{v \in valence} \epsilon_i |\phi_v\rangle \langle \phi_v| + \sum_{a \in virtual} \epsilon_a |\phi_a\rangle \langle \phi_a|$$

- Write $|\phi_v\rangle = |\tilde{\phi}_v\rangle - \sum_{i \in core} |\phi_i\rangle \langle \phi_i | \tilde{\phi}_v\rangle$ with a pseudo-orbital $|\tilde{\phi}_v\rangle$
- Insert this is $\hat{F}|\phi_v\rangle = \epsilon_v |\phi_v\rangle$:

$$\hat{F}|\tilde{\phi}\rangle - \sum_{i \in core} \langle \phi_i | \tilde{\phi}_v \rangle (\epsilon_v - \epsilon_i) |\phi_i\rangle = \epsilon_v |\tilde{\phi}_v\rangle$$

- Additional potential $W_{PK}(\vec{r}) = - \sum_{i \in core} \langle \phi_i | \tilde{\phi}_v \rangle (\epsilon_v - \epsilon_i) \frac{\phi_i(\vec{r})}{\phi_v(\vec{r})}$
- Resulting equations: $[\hat{F} + W_{PK}(\vec{r})] |\tilde{\phi}_v\rangle = \epsilon_v |\tilde{\phi}_v\rangle$
- Problem: what has to be known in advance ?

Model potentials

S.Huzinaga, L.Seijo, Z.Barandiarán, M.Klobukowski, J.Chem.Phys., **86** (1986) 2132
Valence-only **atomic** Hamiltonian as

$$\hat{H} = \sum_{i=1}^N \hat{h}(i) + \sum_{i>j}^N \frac{1}{r_{ij}}$$

One-electron operator

$$\hat{h} = -\frac{1}{2}\Delta - \frac{Z - Z_{\text{core}}}{r} + \hat{V}_{\text{Coul}} + \hat{V}_{\text{Exch}} + \hat{P}$$

- Projector $\hat{P} = -2 \sum_{c \in \text{core}} \epsilon_c |\phi_c\rangle \langle \phi_c|$ shifts all parts of core orbitals to $-2\epsilon_c \gg 0$
- Coulomb term $\hat{V}_{\text{Coul}} = -\frac{Z_{\text{core}}}{r} + 2 \sum_{c \in \text{core}} \hat{J}_c$ with $\langle \phi_i | \hat{J}_c | \phi_j \rangle = (ij|cc)$.
- Exchange term $\hat{V}_{\text{Exch}} = - \sum_{c \in \text{core}} \hat{K}_c$ with $\langle \phi_i | \hat{K}_c | \phi_j \rangle = (ic|cj)$.

- p. 164

- p. 164

Model potentials

Nothing gained yet

- Approximate the Coulomb term

$$\hat{V}_{\text{Coul}} \approx \hat{V}_{\text{Coul}}^{\text{MP}} = \sum_k A_k e^{-\alpha_k r^2} \times \frac{1}{r}$$

(determine A_k, α_k through fit \rightarrow density fitting)

- Exchange term via atomic matrix elements

$$\hat{V}_{\text{Exch}} \approx \hat{V}_{\text{Exch}}^{\text{MP}} = \sum_{\ell} \sum_{m=-\ell}^{\ell} \sum_{a,b} |\phi_{a,\ell,m}\rangle \langle \phi_{a,\ell,m}| A_{\ell;a,b} \langle \phi_{b,\ell,m}|$$

with a set of auxiliary functions $\phi_{a,\ell,m}$. Matrix elements $A_{\ell;a,b}$ from $S^{-1} \hat{V}_{\text{Exch}} S^{-1}$ in the auxiliary basis.

- Atomic calculation produces from the core orbitals all matrix elements of \hat{P} , $\hat{V}_{\text{Coul}}^{\text{MP}}$ and $\hat{V}_{\text{Exch}}^{\text{MP}}$

- p. 164

- p. 174

Model potentials

Molecular valence-only Hamiltonian

$$\hat{H} = \sum_{i=1}^N \hat{h}(i) + \sum_{i>j}^N \frac{1}{r_{ij}} + \sum_{I>J} V_{IJ}(R_{IJ})$$

- One-electron operator

$$\hat{h} = -\frac{1}{2}\Delta - \sum_I \frac{Z_I - Z_{\text{core},I}}{|\vec{R}_I - \vec{r}|} + \sum_I [\hat{V}_{\text{Coul},I} + \hat{V}_{\text{Exch},I} + \hat{P}_I]$$

- Internuclear repulsion term

$$V_{IJ}(R_{IJ}) = \frac{(Z_I - Z_{\text{core},I})(Z_J - Z_{\text{core},J})}{R_{IJ}}$$

- No multicenter contributions $\langle \phi_i | \hat{V}_{\text{Coul}}^I | \phi_j \rangle$

- p. 186

- p. 186

Model potentials

The procedure:

- Initial atomic calculations (fast)
- Generation of the integrals over the potential contributions from the core orbitals
- Molecular calculation with valence electrons only
- Reproduces the complete valence orbitals and energies
- 4-index transformation and correlation calculation as for the frozen-core case
- Building block algorithms

- p. 186

- p. 204

Pseudopotentials

- AIMP need full atomic basis, for expressing the operators and the nodal structure of the orbitals.
- Simpler: nodeless pseudo-orbitals.
- No need for steep functions (core electrons), all can go into the valence polarization and correlation functions

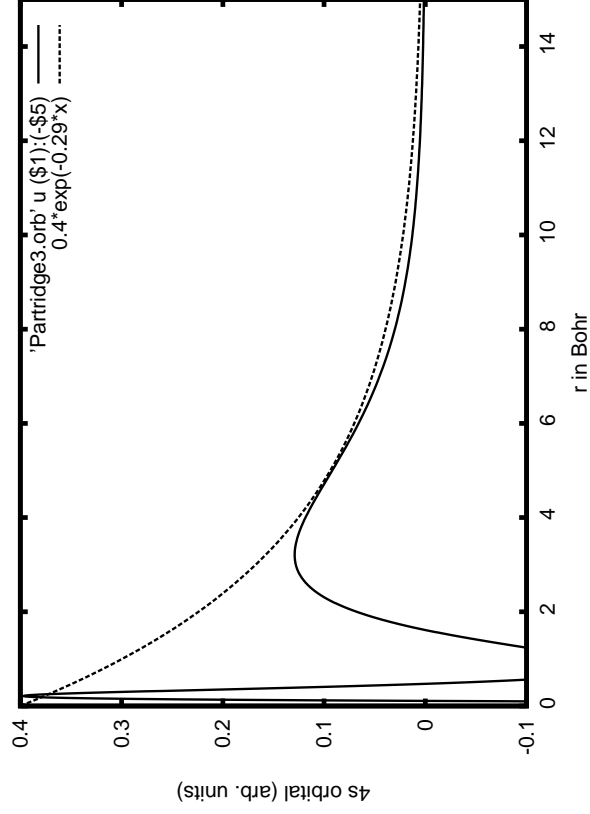
First published: *H.Hellmann, J.Chem.Phys, 5 (1938) 61*

For potassium a preliminary calculation suggested the expression $-1/r + (2.74/r)e^{-1.18r}$ for the complete potential for the valence electron, and the corresponding eigenfunction $\psi \sim e^{-0.29r}$ (approximated by means of the Ritz method expressed in atomic units). Then the Heitler-London method will give for K_2 an equilibrium distance of about 4Å (exp.: 3.9Å) and an energy of about 37 percent of the experimental value. It is this result which agrees very well with the results obtained by James⁸ for Li_2 who considered the effects produced by closed shells in detail. We must also

- p. 216

- p. 224

Pseudopotentials

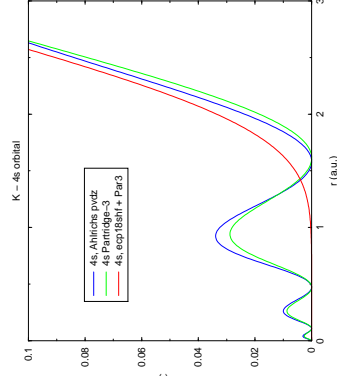
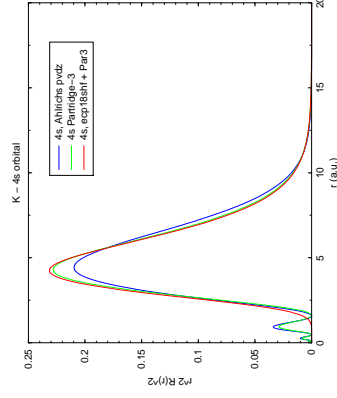


- p. 216

- p. 224

Pseudopotentials

- Shape-consistent pseudopotentials: Hay & Wadt, Durand & Barthelat: orbitals should reproduce the valence orbitals and orbital energies in the best possible way.
- Energy-consistent pseudopotentials: Stuttgart (H.-W.Preuss, M.Dolg etc.): the energy difference of different atomic states should be reproduced in the best possible way.
- Both: nodeless pseudo-orbitals.



Pseudopotentials

- Shape-consistent pseudopotentials: Hay & Wadt, Durand & Barthelat: orbitals should reproduce the valence orbitals and orbital energies in the best possible way.
- Energy-consistent pseudopotentials: Stuttgart (H.-W.Preuss, M.Dolg etc.): the energy difference of different atomic states should be reproduced in the best possible way.
- Both: nodeless pseudo-orbitals.

Analytical form of the potential:

$$V_{PP}(r) = \underbrace{-\frac{Z - Z_{core}}{r}}_{\text{Coulomb term}} + \underbrace{\sum_i d_i r^{n_i} e^{-a_i r^2}}_{\text{local term}} + \underbrace{\sum_{\ell} \left(\sum_i d_{i,\ell} r^{n_{i,\ell}} e^{-a_{i,\ell} r^2} \right) |P_{\ell}\rangle \langle P_{\ell}|}_{\text{semi-local term}}$$

Shape-consistent pseudopotentials

Ph.Durand, J.-C.Barthelat, Theor.Chim.Acta, **38** (1975) 283
 J.-C.Barthelat, Ph.Durand, A.Serafini, Mol.Phys., **33** (1977) 159

$$\hat{F}|\phi_i\rangle = \epsilon_i |\phi_i\rangle$$

should coincide with the equation for the pseudo orbital

$$\left(-\frac{1}{2}\Delta + \hat{V}_{\text{Coul}} + \hat{V}_{\text{Exch}} + \hat{W}_{\text{ps}}\right)|\phi'_i\rangle = \epsilon_i |\phi'_i\rangle$$

with a pseudopotential \hat{W}_{ps} of the form $\hat{W}_{\text{ps}} = -\frac{Z}{r} + \sum_{\ell} W_{\ell}(r) \hat{P}_{\ell}$

$$W_{\ell}(r) = \frac{C}{r} e^{-\alpha r^2}$$

$$W_{\ell}(r) = \left(\frac{C_1}{r^2} + C_2 r^2\right) e^{-\alpha r^2} \quad (1)$$

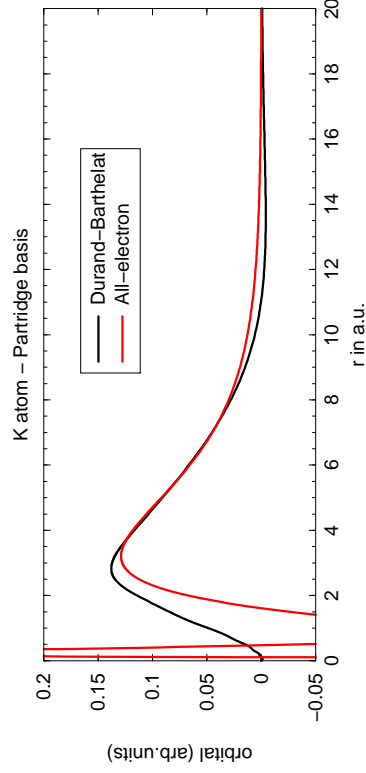
The simpler form applies when there is no inner core orbital of the same ℓ value. s, p, d projectors, obtained via corresponding atomic valence states.

- p. 276

Shape-consistent pseudopotentials

- Atomic ground state or singly-excited valence states
- Minimize operator norm

$$\|O\| = \sqrt{\langle \phi_i | \langle \phi'_i | \langle \phi'_i | - \epsilon_i | \phi_i \rangle \langle \phi_i | \rangle^2 | \phi_i \rangle} \quad (3)$$



- p. 276

- p. 286

Shape-consistent pseudopotentials,II

P.J.Hay, W.R.Wadt, J.Chem.Phys., **82** (1985) 270, 284, 299

- (1) The “core” orbitals to be replaced and the remaining “valence” orbitals are defined.
- (2) Numerical valence orbitals (ϕ_i) are obtained from self-consistent (nonrelativistic or relativistic) Hartree–Fock calculations for $l = 0, 1, \dots, L$, where L , in general, is one greater than the highest angular momentum quantum number of any core orbital.
- (3) Smooth, nodeless pseudo-orbitals ($\hat{\phi}_i$) are derived from the Hartree–Fock orbitals (ϕ_i) in a manner so that $\hat{\phi}_i$ behave as closely as possible to ϕ_i in the outer, valence region of the atom.
- (4) Numerical effective core potentials U_l are derived for each l by demanding that $\hat{\phi}_i$ is a solution in the field of U_l with the same orbital energy ϵ_l as the orbital ϕ_i .
- (5) The numerical potentials are fit in analytic form with Gaussian functions. The total potential is represented as

$$U(r) = U_L(r) + \sum_{l=0}^{L-1} [U_l(r) - U_L(r)] \hat{P}_l \quad (5)$$

- (6) The numerical pseudo-orbitals are also fit with Gaussian functions to obtain basis sets for molecular calculations.

– p. 304

– p. 314

Shape-consistent pseudopotentials,II

Determination of the pseudo-orbitals: smooth function of the form

$$\phi'_l(\vec{r}) = \begin{cases} r^{\ell+3} \sum_{i=0}^4 a_i r^i & r < r_{cut} \\ \phi(\vec{r}) & \text{outside} \end{cases}$$

Inversion of the radial Schrödinger equations: we know the function and the eigenvalues but not the potential:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2} + U_\ell(r) + \tilde{V}_{val} \right] \phi'_\ell(r) = \epsilon_\ell \phi'_\ell(r)$$

with the valence potential $\tilde{V}_{val} = \sum_i a_i J[\phi'_i] - b_i K[\phi'_i]$

$$U_\ell(r) = \epsilon_\ell - \frac{\ell(\ell+1)}{2r^2} + \frac{Z}{r} + \frac{1}{2} \frac{(d^2 \phi_\ell(r)/dr^2)}{\phi_\ell(r)} - \tilde{V}_{val}$$

- The pseudo-orbital MUST be nodeless
- $U_\ell(r)$ determined pointwise, result fitted to Gaussians

– p. 304

– p. 324

Energy-consistent pseudopotentials

H.Stoll, P.Fuentealba, P.Schwerdtfeger, J.Flad, L.v.Szentpály, H.-W.Preuss, J.Chem.Phys., 81 (1984) 2732

- Parameters to reproduce energy differences between atomic states (sometimes hundreds!)
- Numerical Hartree-Fock calculations
- Semi-local form

$$V_{SCF} = \sum_{\ell} \left(\sum_i d_{i,\ell} e^{-a_{i,\ell} r^2} \right) |P_{\ell}\rangle \langle P_{\ell}|$$

- Whole periodic table covered
- Large basis sets provided
- Incorporate scalar-relativistic effects

- p. 334

- p. 344

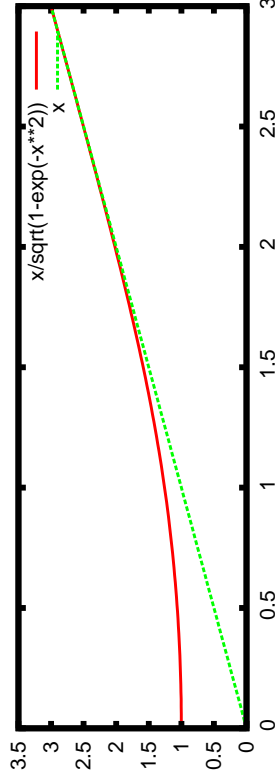
Energy-consistent pseudopotentials

Alkalines, Cu (s1 ground state configuration)

- Pseudopotential should reproduce SCF ionization energies of the excited states (Koopmans theorem): V_{SCF}
- Experimental ionization energies of excited states: $V_{pol} = V - V_{SCF}$

$$V_{Pol} \text{ of the form } V_{Pol} = -\frac{1}{2}\alpha_D \vec{f} \left(\frac{\vec{r}}{\sqrt{1 - \exp(-\delta r^2)}} \right)$$

- \vec{f} field produced at the core by the electron at position \vec{r}
- α_D dipole polarizability of the core, δ cut-off parameter



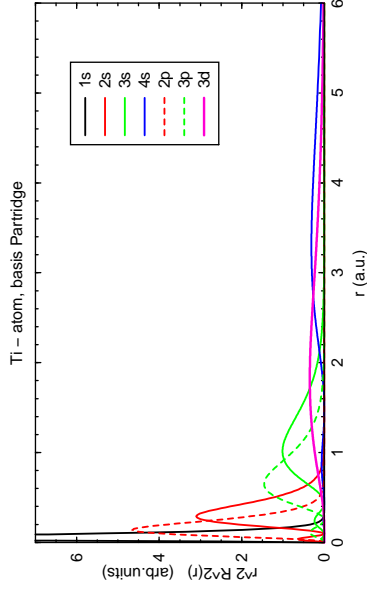
- p. 334

- p. 354

Energy-consistent pseudopotentials

Transition metals: several *s*, *d* electrons

- *3d* electrons in the same region as *3s*, *3p* electrons

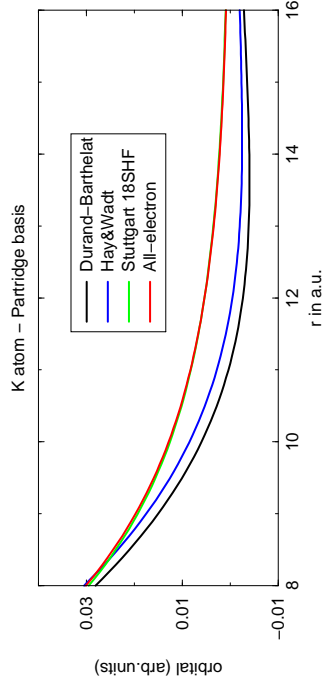
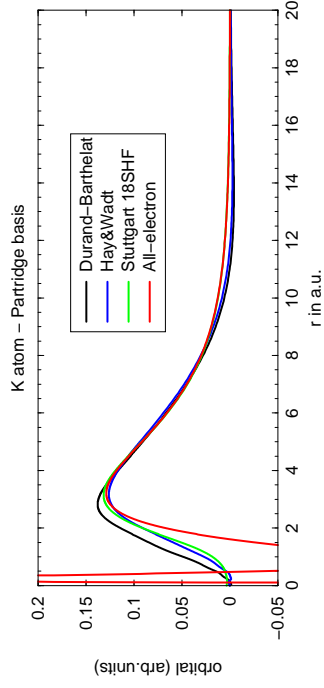


- Ti^0 has a different core than Ti^{3+}
- Large core \leftrightarrow Small core

- p. 364

- p. 374

Energy-consistent pseudopotentials



- p. 364

- p. 384

Example I⁻

Iodine $Z = 53$, $5s^2 5p^5$

- Large core: 46 electrons, small core 28 electrons
- Orbital energies

| | 5s (a.u.) | 5p (a.u.) |
|------------------|-----------|-----------|
| All electron | -0.5566 | -0.1291 |
| Durand-Barthelat | -0.5533 | -0.1254 |
| Hay & Wadt | -0.5948 | -0.1260 |
| Stuttgart (LC) | -0.6065 | -0.1258 |

Bond distance in H-I (experimental value: 1.609 Å)

| | Hartree-Fock (Å) | MP2 (Å) |
|------------------|------------------|---------|
| All-electron | 1.607 | 1.613 |
| Durand-Barthelat | 1.619 | 1.629 |
| Hay & Wadt | 1.595 | 1.597 |
| Stuttgart LC | 1.602 | 1.612 |
| Stuttgart SC | 1.600 | 1.606 |

- p. 386

- p. 406

Example I⁻

Iodine $Z = 53$, $5s^2 5p^5$

- Large core: 46 electrons, small core 28 electrons
- Orbital energies

| | 5s (a.u.) | 5p (a.u.) |
|------------------|-----------|-----------|
| All electron | -0.5566 | -0.1291 |
| Durand-Barthelat | -0.5533 | -0.1254 |
| Hay & Wadt | -0.5948 | -0.1260 |
| Stuttgart (LC) | -0.6065 | -0.1258 |

Tri-iodide ion I_3^- , linear molecule, 160 electrons

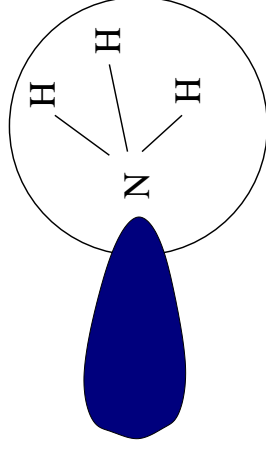
| | Hartree-Fock | MP2 |
|------------------|--------------|------|
| All-electron | 2.78 | 2.92 |
| Durand-Barthelat | 2.99 | 2.97 |
| Hay & Wadt | 2.95 | 2.92 |
| Stuttgart LC | 2.96 | 2.94 |

- p. 386

- p. 406

Beyond: group potentials, total ion potentials

- Replace not only an atomic core, but a whole group through a pseudopotential
- Not any more spherical
- Maintains the volume of the group



- Ionic situations (solids): K^+ , Na^+ , Ti^{4+} , Cl^- , F^-
- No valence electrons for chemical bonding
 - Cations: large-core pseudopotentials
 - Anions: more difficult, e.g. O^{2-} not stable

- p. 426

- p. 446

- p. 436