

## 7 Pseudopotentials

### 7.1 Introduction

Heavy elements are the nightmare of theoreticians.

- Many electrons
- Many orbitals
- Relativistic dynamics

Solution: Find a *pseudopotential* with a ground state which is the lowest needed valence orbital.

- **Local PP** (the same for all values of  $l$ )
- **Semi-local PP** (different radial part for different values of  $l$ );

$$V_l = \mathcal{P}_l V_l(r) \mathcal{P}_l, \quad (7.1)$$

$$\mathcal{P}_l = \sum_{m=-l}^l |lm\rangle \langle lm|. \quad (7.2)$$

Works.

### 7.2 A bit of history

- **H. Hellmann**, "Quantenchemie" (1937), p. 111–. The *Zusatzpotential* for alkali metals

$$U(r) = -\frac{1}{r} + \frac{A}{r} e^{-2\kappa r} \quad (7.3)$$

- **P. Gombás**, *Z. Phys.* **94** (1935) (?) 473,479.  
"Pseudopotentiale", Springer, Wien (1967).  
"Ein Besetzungsverbotpotential".
- A historical wandering: **Phillips-Kleinman**, *Phys. Rev.* **116** (1959) 287.

$$(T + V)\psi_i = \varepsilon_i \psi_i, \quad (7.4)$$

$$V(r) = \frac{(\varepsilon_i - T)\psi_i(r)}{\psi_i(r)}. \quad (7.5)$$

Right  $\varepsilon_i$ , wrong norm of  $\psi$ .

- Fix: **shape-consistent PP**, **norm-conserving PP**. A discussion about which term was in use first is reproduced in figure (7.1) (P. Pyykkö, private communication to **R. Nieminen**, May 13, 1994).

- An own pseudo-potential for the spin-orbit interaction:

$$V^{\text{SO}}(r) = \sum_{l=1}^{l_{\text{max}}} \frac{2\Delta V_l(r)}{2l+1} \mathcal{P}_l \cdot \underline{s} \mathcal{P}_l. \quad (7.6)$$

$$\Delta V_l(r) = V_{l,l+\frac{1}{2}}(r) - V_{l-\frac{1}{2}}(r) \quad (7.7)$$

$$= \sum_k \Delta A_{lk} e^{-a_{lk} r^2} \quad (7.8)$$

**P.A. Christiansen, Y.S. Lee, K.S. Pizer** *J. Chem. Phys.* **71** (1979) 4445.

**P. Hafner, W.H.E. Schwarz** *Chem. Phys. Lett.* **65** (1979) 537.

- The electric polarizability of the ionic core, and the core-valence correlation energy.

$$V_{\text{CPP}} = -\frac{1}{2} \sum_{\lambda} \alpha_{\lambda} (\bar{f}_{\lambda})^2 \quad (7.9)$$

Here  $\alpha_{\lambda}$  is the polarizability of core  $\lambda$  and  $\bar{f}_{\lambda}$  the electric field seen by the core  $\lambda$ .

**P. Fuentealba**, Thesis, Stuttgart (1984)

**W. Müller, J. Flesch, W. Meyer**, *J. Chem. Phys.* **80** (1984) 3297, 3311.

### 7.3 Where to get pseudopotentials

- **USA:**
  - K.S. Pitzer
  - Los Alamos (Hay & Wadt)
  - P.A. Christiansen
  - W. Ermler
  - W.J. Stevens (ECP=PP)
- **Canada, Sweden, Spain:** Huzinaga, Wahlgren, nodal model potentials.
- **Germany:** Stuttgart (Dolg, Stoll, Schwerdtfeger, ...) "Energy consistent PP".  
[www.theochem.uni-stuttgart.de](http://www.theochem.uni-stuttgart.de)
- **France:** Toulouse (Daudley, Teichteil, ...)

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S: History of pseudopotentials

Dear Risto,

As you may recall we had some time ago a friendly "who was first" discussion on the history of the "shape-consistent" or "norm-conserving" pseudopotentials. The former name is used in chemistry and the latter in physics; the common feature of both is that the pseudo wave function reproduce the full wave function in the valence region. (i)

At the workshop of Pseudopotentials of the REHE programme of ESF in Toulouse on Monday, I asked the members of the conference how they thought that these ideas were originally developed.

Apparently the first article was /1/ in 1975. The idea (i) is clearly stated in Fig. 2 and pp. 288-.

According to Walter Ermler, who was at Berkeley in the late 1970'ies, there was communication between the chemists, like him and the physicists, like Dr. A. Zunger, working with M. Cohen. Anecdotally, "we were rather shouting at each other than collaborating", though.

The first paper from Berkeley/Chemistry seems to be /2/. It quotes /1/. The Acknowledgement of /2/ thanks A. Zunger for a preprint of /3/, "in the revision to final form of this manuscript", and also L. Kahn for private communications on his work. Thus the first papers /2, 3/ and the Physics and Chemistry efforts indeed seem entirely parallel. None of the papers /1-3/ uses any particular name for the idea.

In his review /4/ Kahn quotes for the 'shape-consistent' idea (i), his eq. (33), also /5, 6/. Kahn et al. /7/ also clearly discuss the idea (i) in their II.B.ii, without quoting /1/.

Hamann et al. /6/ have the title 'Norm-conserving pseudopotentials' and quote /3, 5/ but not /1, 7/.

Conclusion: The work in the references /1, 7 5/ seems to precede that in ref. /3, 6/. The name 'norm-conserving' from 1979 may be older than the name 'shape-consistent', whose exact origin I have not found. I believe that it was used in the Los Alamos workshop on the subject in 1981.

1. Ph. Durand and J.-C. Barthelat, Theor. Chim. Acta 38 (1975) 283-202.
2. P.A. Christiansen, Y.S. Lee and K.S. Pitzer, J. Chem. Phys. 71 (1979) 4445-4450.
3. A. Zunger, J. Vac. Sci. Technol. 16 (1979) 1337-1438.
4. L. Kahn, Int. J. Quantum Chem. 25 (1984) 149-183.
5. A. Redondo, W.A. Goddard III and T.C. McGill, Phys. Rev. B 15 (1977) 5038-5048. Check ref. 6-7 there.
6. D. R. Hamann, M. Schluter and C. Chiang, Phys. Rev. Letters 43 (1979) 1494-1497.
7. L.R. Kahn, P. Baybutt and D.G. Truhlar, J. Chem. Phys. 65 (1976) 3826-3853.

Figure 7.1: e-mail, May 13, 1994

