

# **Effective Core Potentials**

## **– 70 Years of Development –**

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Hellmann Memorial Meeting  
Bonn, 2003-07-26

# Overview

Fundamentals of electronic structure calculations

The idea of an effective core potential (ECP)

Various types of effective core potentials

Recent extensions of the ECP idea

Summary

# Fundamentals

# Fundamentals of electronic structure calculations

Consider stationary (i. e. timeindependent) states of a system (atom, molecule, ..., crystal) with  $n$  electrons and  $K$  space-fixed nuclei.

Solve the Schrödinger equation:

$$\mathcal{H} \Psi_k = E_k \Psi_k$$

for  $E_k$  and  $\Psi_k$ , where  $k = (0), 1, 2, \dots$  (under some boundary conditions  $\rightarrow$  eigenvalue problem).

$\mathcal{H}$	— Hamilton operator ('defines' the system)
$E_k$	— state energies (eigenvalues)
$\Psi_k = \Psi_k(\mathbf{x}_1, \dots, \mathbf{x}_n)$	— state functions ('wave functions', eigenfunctions, or eigenvectors)
$\mathbf{x} = (\mathbf{r}, \sigma)$	— combined space ( $\mathbf{r}(x, y, z)$ ) and spin ( $\sigma$ ) coordinates

Zero-, one-, and two-electron parts of the Hamilton operator (in atomic units):

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2$$

$$\mathcal{H}_0 = \sum_{\lambda < \mu}^K \frac{Z_\lambda Z_\mu}{R_{\lambda\mu}} \text{ — nuclear repulsion } (Z_\lambda \text{ nuclear charge, } R_{\lambda\mu} \text{ internuclear distance)}$$

$$\mathcal{H}_1 = \sum_{i=1}^n h(i) \text{ — one-electron part } (h \text{ is a one-electron operator)}$$

$$\mathcal{H}_2 = \sum_{i < j}^n g(i, j) \text{ — two-electron part } (g \text{ is a two-electron operator)}$$

State functions  $\Psi_k$  can be expanded in antisymmetrized products  $\Phi_j$  of single particle functions  $\psi_i(\mathbf{x})$  (spin orbitals or spinors), e. g.

$$\Psi_k = \sum_j C_{jk} \Phi_j$$
$$\Phi_j = \frac{1}{\sqrt{n!}} |\psi_{j_1} \psi_{j_2} \cdots \psi_{j_{n-1}} \psi_{j_n}|$$

$\Phi_j$  — Slater determinants

This expression automatically fulfills the Pauli principle for fermions (e. g. electrons)

$$\Phi_j(\dots, \mathbf{x}_a, \dots, \mathbf{x}_b, \dots) = -\Phi_j(\dots, \mathbf{x}_b, \dots, \mathbf{x}_a, \dots)$$

while for bosons (e. g.  $\alpha$ -particle,  ${}^4\text{He}$ )

$$\Phi_j(\dots, \mathbf{x}_a, \dots, \mathbf{x}_b, \dots) = +\Phi_j(\dots, \mathbf{x}_b, \dots, \mathbf{x}_a, \dots)$$

A simple example:  $n = 2$

$$\begin{aligned}\Phi(\mathbf{x}_1, \mathbf{x}_2) &= \frac{1}{\sqrt{2}} |\psi_k \psi_l| = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_k(\mathbf{x}_1) & \psi_k(\mathbf{x}_2) \\ \psi_l(\mathbf{x}_1) & \psi_l(\mathbf{x}_2) \end{vmatrix} \\ &= \frac{1}{\sqrt{2}} (\psi_k(\mathbf{x}_1)\psi_l(\mathbf{x}_2) - \psi_l(\mathbf{x}_1)\psi_k(\mathbf{x}_2)) \\ &= -\Phi(\mathbf{x}_2, \mathbf{x}_1)\end{aligned}$$

→ electrons are indistinguishable ('each electron uses every single particle function')

For the ground state of the helium atom, He  $1s^2 \ ^1S$ , choose:

$$\psi_k(\mathbf{x}) = \psi_{1s}(\mathbf{r})\alpha \qquad \psi_l(\mathbf{x}) = \psi_{1s}(\mathbf{r})\beta$$

(or vice versa), and determine  $\psi_{1s}(\mathbf{r})$ .

Determination of the 'best' set of single electron functions  $\{\psi_j\}$  from the variational principle, applied to the energy expectation value

$$E[\{\psi_j\}] = \langle \Psi_k | \mathcal{H} | \Psi_k \rangle \quad \text{with} \quad \langle \Psi_k | \Psi_k \rangle = 1$$

$$E_k \leq \min_{\{\psi_j\}} E[\{\psi_j\}]$$

under the orthogonality and normalization conditions  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$

→ Euler-Lagrange equations

$$\frac{\delta E}{\delta \psi_j} = 0$$

Their precise form depends on the underlying 'physical picture' (e. g. non-relativistic / relativistic treatment) and the form of the state function  $\Psi_k$  involved.



Canonical Fock equations for the spatial part  $\psi_j(\mathbf{r})$  of single electron functions (closed-shell case, non-relativistic treatment):

$$\frac{\delta E}{\delta \psi_j} = 0 \quad \Rightarrow \quad (\mathcal{F} - \varepsilon_j)\psi_j = 0$$

$$\mathcal{F} = h + \sum_i (2\mathcal{J}_i - \mathcal{K}_i)$$

$$\mathcal{J}_i \psi_j(\mathbf{r}) = \psi_j(\mathbf{r}) \int d\tau' \psi_i^*(\mathbf{r}') g \psi_i(\mathbf{r}')$$

$$\mathcal{K}_i \psi_j(\mathbf{r}) = \psi_i(\mathbf{r}) \int d\tau' \psi_i^*(\mathbf{r}') g \psi_j(\mathbf{r}')$$

with one- and two-electron operators (in atomic units)

$$h = \frac{1}{2}\mathbf{p}^2 + \sum_{\lambda} V_{\text{nuc}}^{\lambda}(\mathbf{r}_{\lambda}) \quad g = \frac{1}{|\mathbf{r} - \mathbf{r}'|}$$

$\mathbf{p} = -i\nabla$  — operator of linear momentum

$V_{\text{nuc}}^{\lambda}(\mathbf{r}_{\lambda})$  — nuclear potential (for point-like nuclei:  $-Z_{\lambda}/r_{\lambda}$ )

$\varepsilon_j$  — orbital energy

$\psi_j$  — orbital (spatial part of the spin orbital)

Relativistic treatment:

One- and two-electron operators

$$h = c\boldsymbol{\alpha} \cdot \mathbf{p} + c^2(\beta - 1_4) + \sum_{\lambda} V_{\text{nuc}}^{\lambda}(\mathbf{r}_{\lambda}) \quad g = \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \text{corrections}$$

4 × 4 Dirac matrices  $\boldsymbol{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$  and  $\beta$

Inclusion of corrections in  $g \longrightarrow$  Gaunt or Breit operators for electron interaction

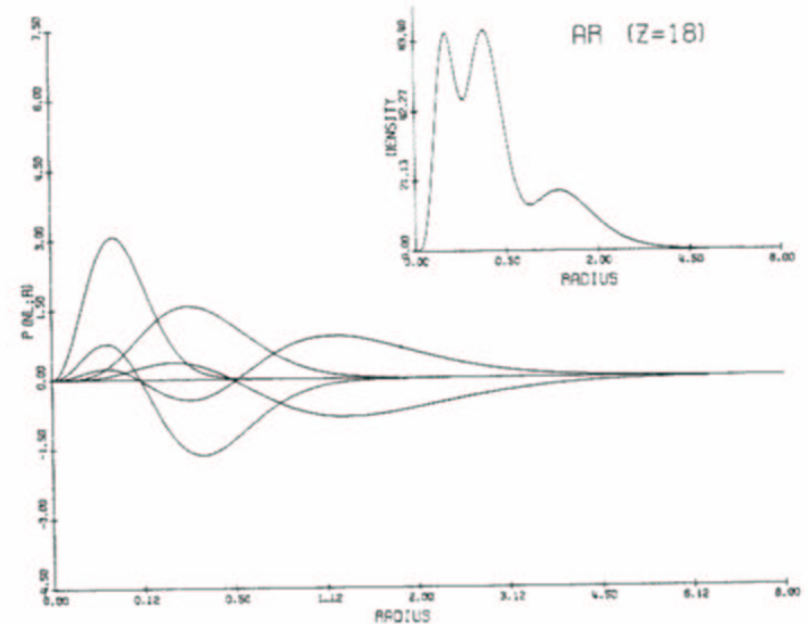
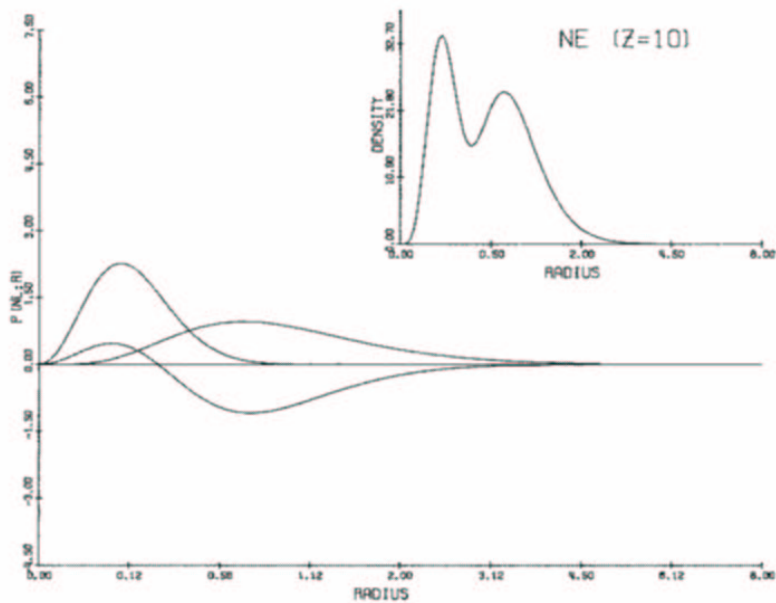
4-component spinor ('single electron function')

$$\psi_j(\mathbf{x}) = \begin{pmatrix} \psi_{1,j}(\mathbf{r}) \\ \psi_{2,j}(\mathbf{r}) \\ \psi_{3,j}(\mathbf{r}) \\ \psi_{4,j}(\mathbf{r}) \end{pmatrix}$$

# Electronic structure of atoms

Spatial part of atomic spin orbitals can be written as

$$\psi_{nlm}(\mathbf{r}) = r^{-1} P_{nl}(r) Y_{lm}(\hat{\mathbf{r}})$$



Ne [<sub>2</sub>He]  $2s^2 2p^6 1S$

Ar [<sub>10</sub>Ne]  $3s^2 3p^6 1S$

From: Charlotte Froese Fischer: *The Hartree-Fock method for atoms*.  
Wiley, New York, 1977

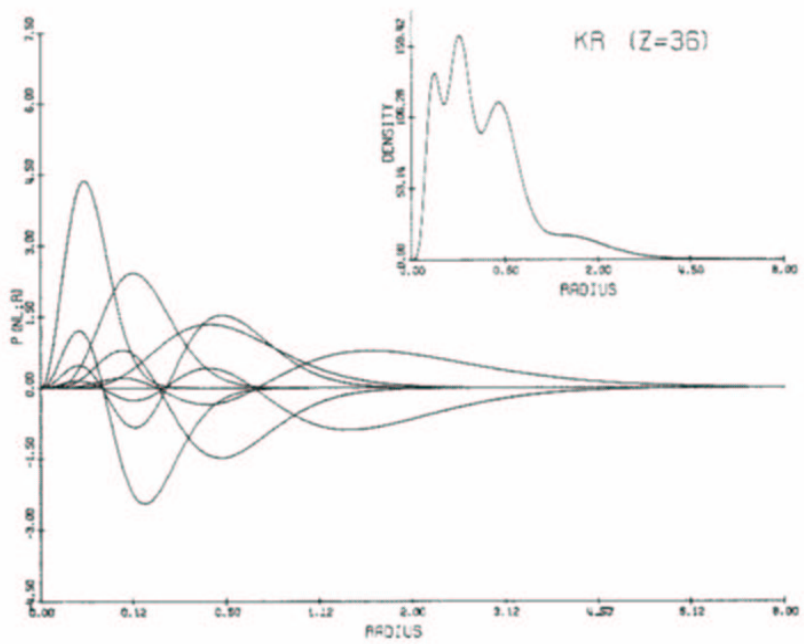


FIGURE 2.3 Hartree-Fock radial functions and radial density functions for Kr.

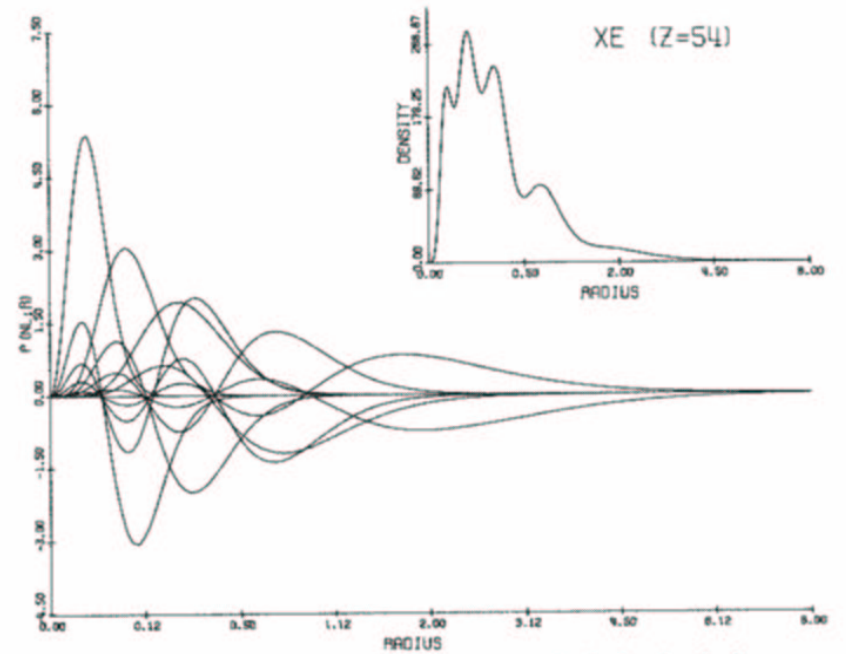
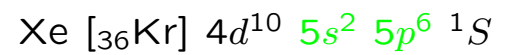
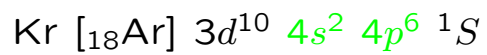
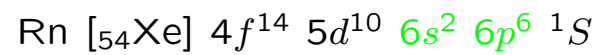
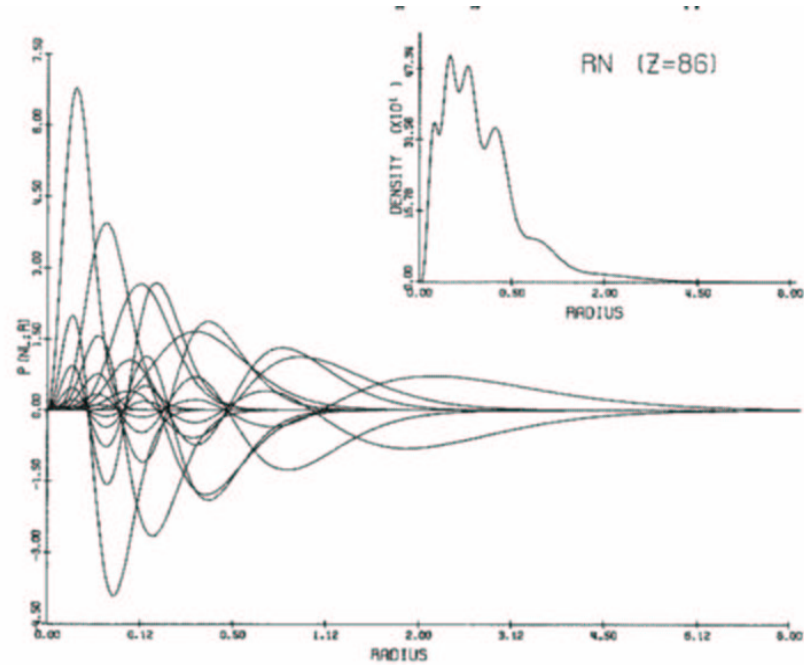


FIGURE 2.4 Hartree-Fock radial functions and radial density functions for Xe.



From: Charlotte Froese Fischer: *The Hartree-Fock method for atoms*.  
 Wiley, New York, 1977



From: Charlotte Froese Fischer: *The Hartree-Fock method for atoms*.  
 Wiley, New York, 1977

**Chemical experience:** Elements from the same group of the periodic table behave similarly in chemical reactions → similar 'valence part'

Is a reduction of our equations to a 'valence system' with only

$$n_v = n - \sum_{\lambda}^K (Z_{\lambda} - Q_{\lambda})$$

electrons possible ( $Q_{\lambda}$  core charges)? Yes, but not rigorously!

For our examples (noble gas atoms):  $ns^2 np^6$ ,  $n_v = 8$

Can one study the influence of the core on the valence part in atoms, and then transfer this knowledge to the study of molecules?

Yes, with very good accuracy for valence part properties!

**Important decision:** Which part becomes the 'core', and what remains for the 'valence system'? (Iterative improvement - starting from the chemist's 'valence system' - is possible)

Valence Hamilton operator (in atomic units):

$$\mathcal{H}_v = V_{cc} + \sum_i^{n_v} h_v(i) + \sum_{i < j}^{n_v} \frac{1}{r_{ij}}$$

$$V_{cc} = \sum_{\lambda < \mu}^K \frac{Q_\lambda Q_\mu}{R_{\lambda\mu}} \text{ — core-core and core-nuclear repulsion}$$

$$h_v(i) = -\frac{1}{2} \nabla_i^2 + U_{cv}(i) \text{ — effective one-electron operator}$$

effective core potential (ECP):

$$U_{cv}(i) = \sum_{\lambda}^K \left\{ -\frac{Q_\lambda}{r_{\lambda i}} + \Delta U_{cv}^\lambda(\mathbf{r}_{\lambda i}) \right\}$$

# The idea of an effective core potential



Г. Гельман / Н. Hellmann (10.06.1934), О комбинированном приближенном расчете проблемы многих электронов / Über ein kombiniertes Störungsverfahren im Vielelektronenproblem, Докл. Акад. Наук СССР / *C. R. (Dokl.) Acad. Sci. URSS* **4** (1934) 442–444 (in Russian), 444–446 (in German).

→ „Zusatzpotential“  $\partial T/\partial \rho$ , derived from Thomas-Fermi theory

H. Hellmann (26.11.1934), A New Approximation Method in the Problem of Many Electrons, *J. Chem. Phys.* **3** (1935) 61.

H. Hellmann (17.12.1934; 03.12.1935), Ein kombiniertes Näherungsverfahren zur Energieberechnung im Vielelektronenproblem, *Acta Physicochim. URSS* **1** (1934/1935) 913–940; Ein kombiniertes Näherungsverfahren zur Energieberechnung im Vielelektronenproblem. II, *Acta Physicochim. URSS* **4** (1936) 225–244.

→ dependence on angular momentum ( $l$ , not  $j = l + s$ )

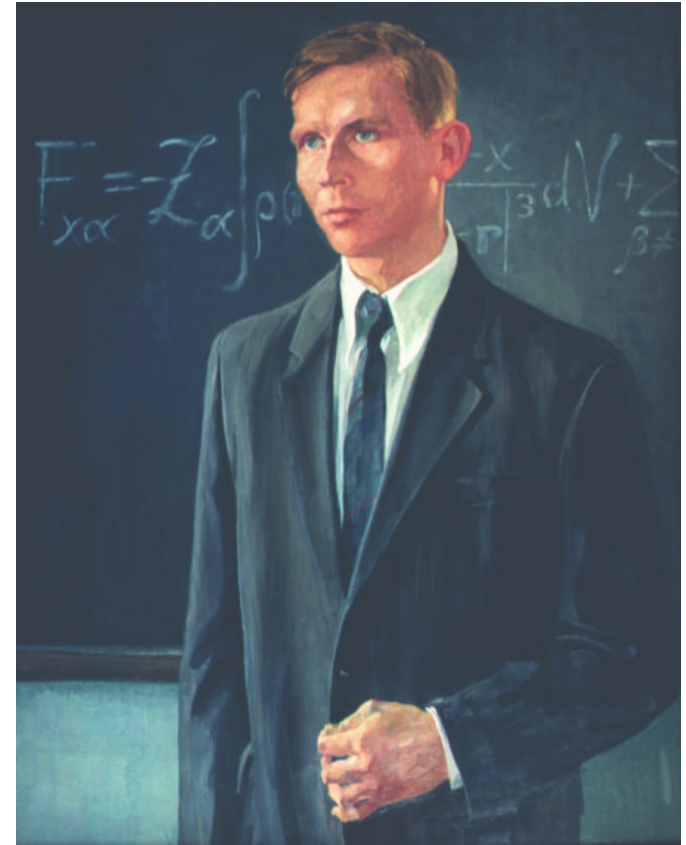
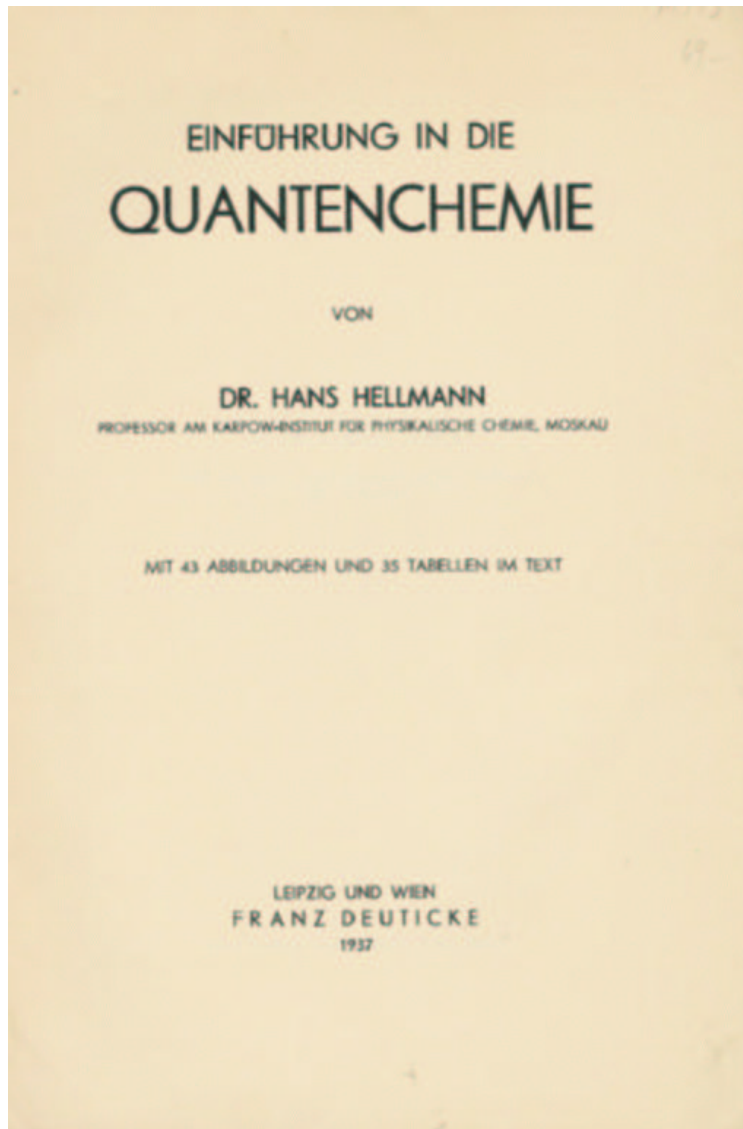
H. Hellmann, W. Kassatotschkin (15.03.1936), Metallic Binding According to the Combined Approximation Procedure, *J. Chem. Phys.* **4** (1936) 324–325.

H. Hellmann, W. Kassatotschkin (16.05.1936), Die metallische Bindung nach dem kombinierten Näherungsverfahren, *Acta Physicochim. URSS* **5** (1936) 23–44.

→ analytic expression with parameters adjusted to experimental atomic excitation energies, application to alkali metals

Г. Гельман (23.10.1936), Квантовая Химия, ОНТИ, Москва, 1937 г.

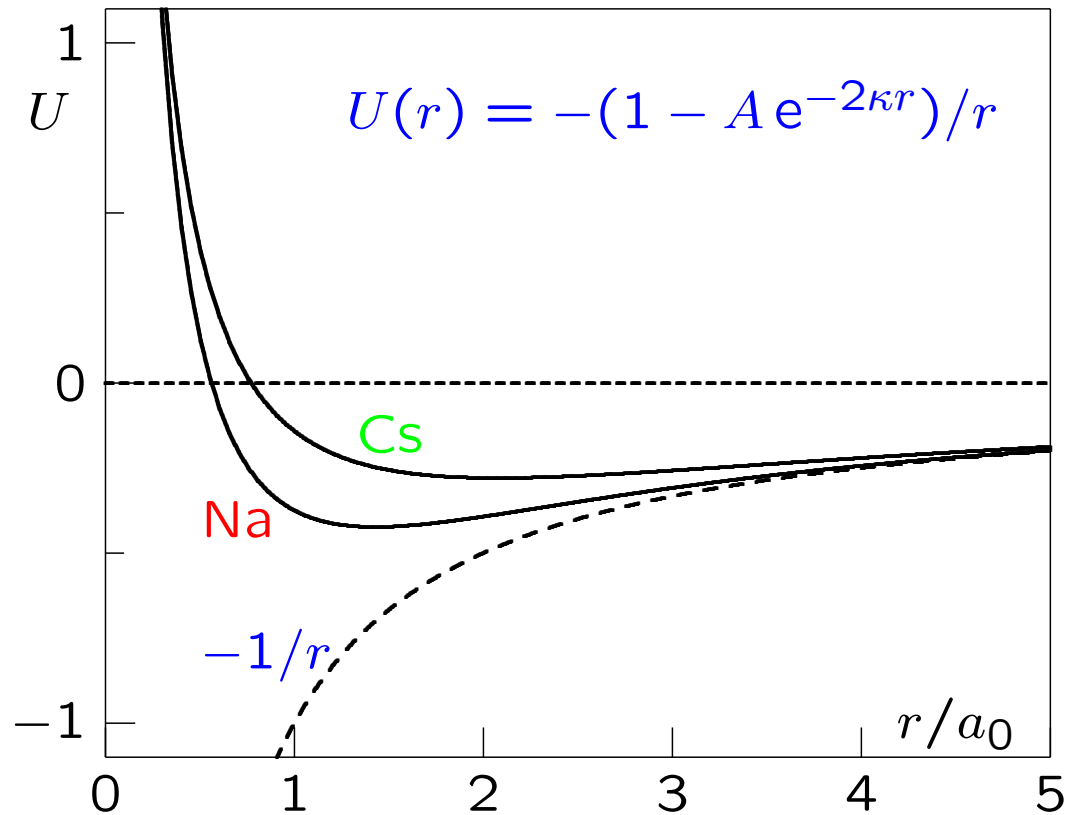
Hans Hellmann (März 1937), Einführung in die Quantenchemie, Deuticke, Leipzig, 1937.



Hans Hellmann  
(1903–1938)

$$U = V_{\text{core}} + \frac{\partial T}{\partial \rho} \quad \longrightarrow \quad U(r) = -\frac{1}{r} + \frac{A}{r} e^{-2\kappa r}$$

Portrait of Hans Hellmann painted by Tatyana Livshits, Moscow, according to a photo taken in 1933



Effective core potential  $U(r)$ , in atomic units, for **sodium** (Na:  $A = 1.826$ ;  $\kappa = 0.536$ ) and **cesium** (Cs:  $A = 1.672$ ;  $\kappa = 0.333$ ), used in this form by Hellmann and Kassatochkin in a study of metallic binding in alkali metals [ H. Hellmann, W. Kassatotschkin: Die metallische Bindung nach dem kombinierten Näherungsverfahren. *Acta Physicochim. U. R. S. S.* **5** (1936) 23–44; parameters adjusted to experimental term energies ].

## Independent parallel development

Paul Gombás (04.03.1935), Über die metallische Bindung, *Z. Phys.* **94** (1935) 473–488.

→ Thomas-Fermi theory applied to the atomic core, using a representation of the core density given by W. Lenz and H. Jensen

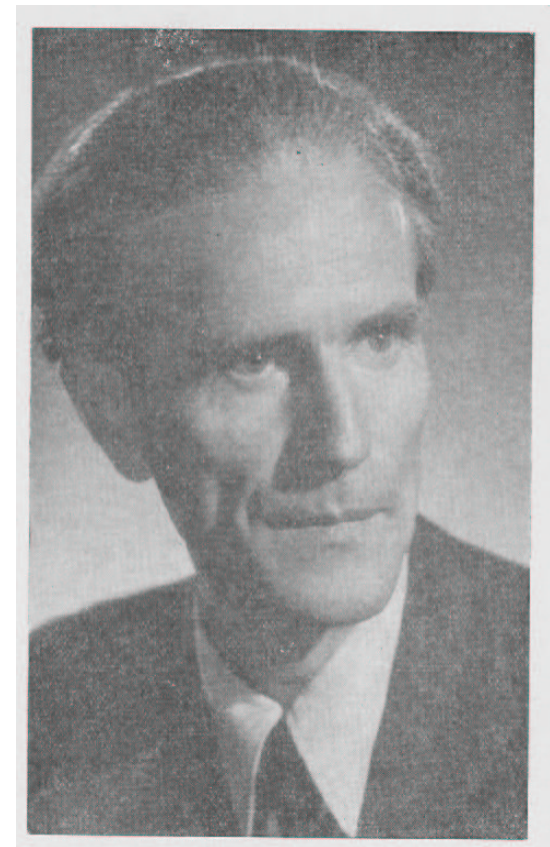
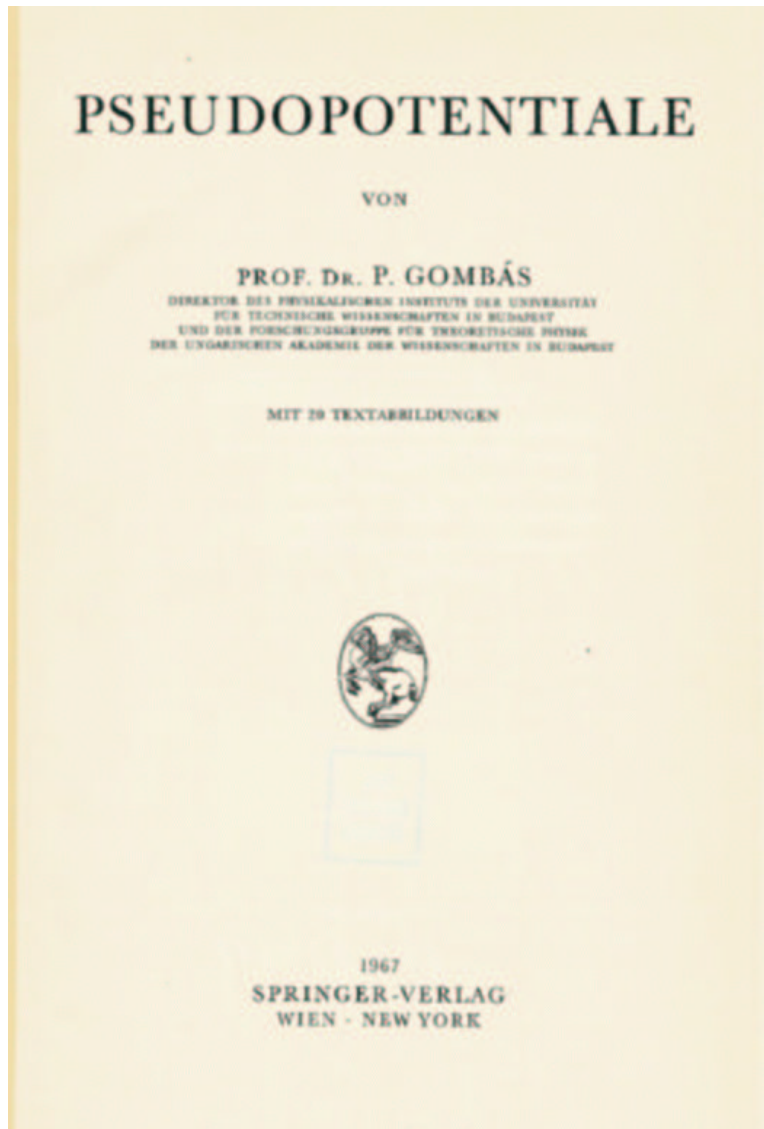
Paul Gombás, Über eine vereinfachte Formulierung der Besetzungsvorschrift der Quantenzustände von Atomen und deren Anwendung zur Bestimmung der Atomterme, *Z. Phys.* **118** (1941/1942) 164–180.

Paul Gombás, Zur Berechnung von Atomtermen, *Z. Phys.* **119** (1942) 318–324.

Paul Gombás, Pseudopotentiale, Springer, Wien, 1967.

\*\*\* Dependence on angular momentum explicitly included (i. e.  $U \rightarrow U_l$ )

\*\*\* Development of  $l$ -dependent potentials for exchange and correlation



Pál Gombás  
(1909–1971)

Photograph taken from obituary written by R. Gáspár, *Acta Phys. Acad. Sci. Hung.* **30** (1971) 109

## Early applications of the Hellmann potential

H. Preuß, Untersuchungen zum kombinierten Näherungsverfahren. *Z. Naturforsch. A* **10** (1955) 365–373

K. Ladányi, Zur Theorie der Edelmetalle, *Acta Phys. Acad. Sci. Hung.* **5** (1955) 361–380

L. Szasz, G. McGinn, Energy-Term Calculations with Hellmann-Type Pseudopotential, *J. Chem. Phys.* **42** (1965) 2363–2370

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***Pseudopotential  
Theory of  
Atoms and  
Molecules***

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*Levente Szasz  
Fordham University*

A WILEY-INTERSCIENCE PUBLICATION  
**JOHN WILEY & SONS**

*New York • Chichester • Brisbane • Toronto • Singapore*

L. Szasz, Pseudopotential Theory of Atoms and Molecules, Wiley, New York, 1985



## Search for a theoretical basis

$$\left(-\frac{1}{2}\nabla^2 + U^{(G)PK}\right) \varphi_k^v = \varepsilon_k \varphi_k^v$$

A complicated operator ( $U^{(G)PK}$ ) appears, which requires full knowledge of the solutions of the all-electron case.

Orbital transformation:

$$\varphi_k^v = \psi_k^v + \sum_{j \in c} c_{jk} \psi_j^c$$

valence orbital (**nodes**)  $\psi_k^v \rightarrow$  pseudo-valence orbital (**nodeless**)  $\varphi_k^v$

- (a) I. Fényes, *Csillagászati Lapok (Budapest)* **6** (1943) 49 (based on Hartree theory);
- (b) P. Szépfalusy, *Acta Phys. Acad. Sci. Hung.* **5** (1955) 325 & **6** (1956) 273  
(based on Hartree-Fock theory);
- (c) E. Antončík, *Czech. J. Phys.* **7** (1957) 118 & **9** (1959) 291;
- (d) J. C. Phillips, L. Kleinman, *Phys. Rev.* **116** (1959) 287 ('**pseudopotential**');
- (e) A. U. Hazi, S. A. Rice, *J. Chem. Phys.* **45** (1966) 3004;  
J. D. Weeks, A. Hazi, S. A. Rice, *Adv. Chem. Phys.* **16** (1969) 283



# Various types of effective core potentials

**Local** operators (multiplicative operator):

$$U(\mathbf{r}) \quad \text{or} \quad U(r)$$

'acts' in the same way onto every function  
determine one function  $U(r)$  (as Hellmann did)

**Semilocal** operators:

$$U^\lambda = \sum_l U_l^\lambda(r) \mathcal{P}_l^\lambda \quad \text{or} \quad U^\lambda = \sum_j U_j^\lambda(r) \mathcal{P}_j^\lambda$$

Projector on angular momentum subspace on center  $\lambda$ , e. g.:

$$\mathcal{P}_l^\lambda = \sum_{m=-l}^l |\lambda l m\rangle \langle \lambda l m| \quad \left( \text{or: } \mathcal{P}_j^\lambda = \sum_{m=-j}^j |\lambda j m\rangle \langle \lambda j m| \right)$$

'acts' in the same way for given angular momentum  
determine one function  $U_l(r)$  for every angular momentum  $l$

**Nonlocal** operators:

$$U^\lambda = \sum_{ij} |\chi_i^\lambda\rangle C_{ij} \langle \chi_j^\lambda|$$

'acts' differently on different functions  
choose / determine a suitable set of functions (a basis)  $\{\chi_i^\lambda(\mathbf{r})\}$

## Important ways to determine $U_l^\lambda$

- (a) Inversion of the Schrödinger equation for the (nodeless) pseudoorbital, subsequent fitting to some useful analytic expression ( $\rightarrow$  shape-consistent)

$$\left(-\frac{1}{2}\nabla^2 + U_l^\lambda\right)\varphi_l = \varepsilon\varphi_l \quad \Rightarrow \quad U_l^\lambda(\mathbf{r}) = \varepsilon + \frac{1}{2}\frac{\varphi_l''}{\varphi_l} \approx \sum_k c_k f_k(\alpha_k, \mathbf{r})$$

- (b) Direct determination or optimization (e. g. via least squares) of the parameters in an analytic expression for  $U_l^\lambda$  with respect to some reference data

$$U_l^\lambda(\mathbf{r}) = \sum_k c_k f_k(\alpha_k, \mathbf{r}) \quad \Rightarrow \quad S = \sum_i w_i (\langle \mathcal{O}^{\text{ECP}} \rangle_i - \langle \mathcal{O}^{\text{ref}} \rangle_i)^2 = \text{min}$$

$$\Rightarrow \quad \{c_k, \alpha_k\}$$

- $\langle \mathcal{O}^{\text{ECP}} \rangle_i$  value of property  $\mathcal{O}$  evaluated with ECP for state  $i$   
 $\langle \mathcal{O}^{\text{ref}} \rangle_i$  reference value of that property for state  $i$

## Shape-consistent pseudopotentials:

$$U^\lambda(\mathbf{r}) = U_L^\lambda(r) + \sum_{l=0}^{L-1} (U_l^\lambda(r) - U_L^\lambda(r)) \mathcal{P}_l^\lambda$$

$$U_L^\lambda(r) = \sum_k A_k r^{n_k} \exp(-\alpha_k r^2)$$

$$U_l^\lambda(r) - U_L^\lambda(r) = \sum_k B_k r^{m_k} \exp(-\beta_k r^2)$$

keep the resulting pseudo-valence orbital  $\varphi^v$  **identical** with the valence orbital  $\psi^v$  **beyond** some matching radius:  $\varphi^v(r) \equiv \psi^v(r)$  for  $r \geq R_c$

determine parameters through inversion of a Schrödinger-type equation

(a) W. A. Goddard III, *Phys. Rev.* **174** (1968) 659

(b) Ph. Durand, J.-C. Barthelat, *Theor. Chim. Acta* **38** (1975) 283

(c) L. R. Kahn, P. Baybutt, D. G. Truhlar, *J. Chem. Phys.* **65** (1976) 3826

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

(e) Hay / Wadt — Christiansen / Ermler / Pitzer — Stevens / Basch / Krauss / Jasien / Cundari

available e. g. from URL <http://www.clarkson.edu/~pac/reps.html>

## Generalized Relativistic Effective Core Potentials (GRECP):

$$\begin{aligned}
 U = & U_{n_v L J}(r) + \sum_{l=0}^L \sum_{j=|l-1/2|}^{j=l+1/2} \left[ U_{n_v l j}(r) - U_{n_v L J}(r) \right] \mathcal{P}_{l j} \\
 & + \sum_{n_c} \sum_{l=0}^L \sum_{j=|l-1/2|}^{j=l+1/2} \left\{ \left[ U_{n_c l j}(r) - U_{n_v l j}(r) \right] \mathcal{P}_{n_c l j} \right. \\
 & \quad \left. + \mathcal{P}_{n_c l j} \left[ U_{n_c l j}(r) - U_{n_v l j}(r) \right] \right\} \\
 & - \sum_{n_c, n'_c} \sum_{l=0}^L \sum_{j=|l-1/2|}^{j=l+1/2} \mathcal{P}_{n_c l j} \left[ \frac{U_{n_c l j}(r) + U_{n'_c l j}(r)}{2} - U_{n_v l j}(r) \right] \mathcal{P}_{n'_c l j}
 \end{aligned}$$

two new terms added to the semi-local form already known  
 requires a technique to invert the Schrödinger equation for valence orbitals **with** nodes  
 the various radial parts, which appear above, are fitted to analytic expressions  
 uses projection operators onto outer core pseudospinors

(a) A. V. Titov, A. O. Mitrushenkov, I. I. Tupitsyn, *Chem. Phys. Lett.* **185** (1991) 330;

(b) N. S. Mosyagin, A. V. Titov, A. V. Tulub, *Phys. Rev. A* **50** (1994) 2239;

(c) A. V. Titov, N. S. Mosyagin, *Int. J. Quantum Chem.* **71** (1999) 359

available from URL <http://qchem.pmpi.spb.ru/publication/recp.html> for Ba, Yb, Hg–Rn

## Energy-consistent pseudopotentials:

$$U^\lambda(\mathbf{r}) = U_L^\lambda(r) + \sum_{l=0}^{L-1} (U_l^\lambda(r) - U_L^\lambda(r)) \mathcal{P}_l^\lambda$$

$$U_L^\lambda(r) = \sum_k A_k r^{n_k} \exp(-\alpha_k r^2)$$

$$U_l^\lambda(r) - U_L^\lambda(r) = \sum_k B_k r^{m_k} \exp(-\beta_k r^2)$$

Determine parameters through optimization w. r. t. observable quantities (e. g. energies, **as Hellmann did** — minimize least squares sum)

Reference data may come from many different sources (e. g. experiment, or various theoretical levels — make an exclusive choice)

Dolg / Schwerdtfeger / Wedig / Stoll / Preuß

available from URL <http://www.theochem.uni-stuttgart.de/pseudopotentials>

## Error analysis for semilocal ECPs

The modern ECP approach relies heavily on error compensation. Some important errors involved are

- (a) frozen core approximation (implicit or explicit assumption of a 'frozen core')
- (b) core valence separation (core and valence part are considered as independent subsystems)
- (c) introduction of effective one-electron operators, replacing in part one- and two-electron operators from the all-electron approach
- (d) (pseudo) orbital transformation (removal of nodal structure of valence orbitals [ not for model potentials ])

For further details see

- (a) W. H. E. Schwarz, *Theor. Chim. Acta* **11** (1968) 307, 377,  
*Acta Phys. Acad. Sci. Hung.* **27** (1969) 391
- (b) T. C. Chang, P. Habitz, B. Pittel, W. H. E. Schwarz, *Theor. Chim. Acta* **34** (1974) 263
- (c) B. Pittel, W. H. E. Schwarz, *Chem. Phys. Lett.* **46** (1977) 121
- (d) T. C. Chang, P. Habitz, W. H. E. Schwarz, *Theor. Chim. Acta* **44** (1977) 61

*ab initio* model potentials (AIMP — non-local ECPs)

$$-\sum_{\lambda} \frac{Z_{\lambda}}{r_{\lambda i}} + \sum_{j \in c} \{2\mathcal{J}_j(i) - \mathcal{K}_j(i)\} = \sum_{\lambda} \left\{ -\frac{Q_{\lambda}}{r_{\lambda i}} + \Delta U_{cv}^{\lambda}(\mathbf{r}_{\lambda i}) \right\}$$

approximate  $\Delta U_{cv}^{\lambda}(\mathbf{r}_{\lambda i})$  by a sum of semilocal and nonlocal terms with adjustable parameters (for every core  $\lambda$ )

$$\begin{aligned} -\frac{Z_{\lambda}}{r_{\lambda i}} + 2 \sum_{c \in \lambda} \mathcal{J}_c(i) - \sum_{c \in \lambda} \mathcal{K}_c(i) = & -\frac{Q_{\lambda}}{r_{\lambda i}} + \sum_k c_k^{\lambda} r_{\lambda i}^{n_k^{\lambda}} \exp(-\alpha_k^{\lambda} r_{\lambda i}^2) \\ & + \sum_{p,q} |\chi_p^{\lambda}\rangle A_{pq}^{\lambda} \langle \chi_q^{\lambda}| + \sum_{c \in \lambda} |\psi_c^{\lambda}\rangle B_c^{\lambda} \langle \psi_c^{\lambda}| \end{aligned}$$

no orbital transformation required — nodal structure of valence orbitals retained

S. Huzinaga, A. A. Cantu, *J. Chem. Phys.* **55** (1971) 5543; V. Bonifacić, S. Huzinaga, *J. Chem. Phys.* **60** (1974) 2779; Y. Sakai, S. Huzinaga, *J. Chem. Phys.* **76** (1982) 2537; M. Klobukowski, *J. Comput. Chem.* **4** (1983) 350; S. Huzinaga, L. Seijo, Z. Barandiarán, M. Klobukowski, *J. Chem. Phys.* **86** (1987) 2132; Z. Barandiarán, L. Seijo, *J. Chem. Phys.* **101** (1994) 4049; C. M. Marian, U. Wahlgren, *Chem. Phys. Lett.* **251** (1996) 357; L. Seijo, Z. Barandiarán, E. Harguindey, *J. Chem. Phys.* **114** (2001) 118

available from URL <http://www.uam.es/quimica/aimp> and  
<http://www.thch.uni-bonn.de/tc/TCB.download.html>



## Additional refinements

Correction for point-like core-core interaction

Core polarization potentials

Spin-orbit interaction potentials

## Correction for point-like core-core interaction

If necessary (e. g. when large-core ECPs are used), one can replace

$$V_{cc} = \sum_{\lambda < \mu}^K \frac{Q_\lambda Q_\mu}{R_{\lambda\mu}} \quad \rightarrow \quad V_{cc} = \sum_{\lambda < \mu}^K \left\{ \frac{Q_\lambda Q_\mu}{R_{\lambda\mu}} + \Delta V_{cc}^{\lambda\mu}(\mathbf{R}_{\lambda\mu}) \right\}$$

and parameterize the correction terms, e. g.

$$\Delta V_{cc}^{\lambda\mu}(\mathbf{R}_{\lambda\mu}) = B_{\lambda\mu} \exp(-b_{\lambda\mu} R_{\lambda\mu})$$

(for each pair of centers  $(\lambda, \mu)$ ).

## Core polarization potentials

To account for (i) core polarization and (ii) (part of) core-valence correlation, one may add:

$$V_{cpp} = -\frac{1}{2} \sum_{\lambda} \alpha_{\lambda} f_{\lambda}^2$$

$\alpha_{\lambda}$  — electric dipole polarizability of core  $\lambda$

$f_{\lambda}$  — electric field at core  $\lambda$ , due to all other cores or nuclei, and all valence electrons (has to include a short-range cutoff)

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

(b) P. Fuentealba, Thesis, Univ. Stuttgart, 1984

## Spin-orbit interaction potentials

$$V_{\text{SO}}^{\lambda}(i) = \sum_{l=1}^{l_{\text{max}}} \frac{2}{2l+1} \Delta U_l^{\lambda}(r_{\lambda i}) \mathcal{P}_l^{\lambda} \mathbf{l}_i \cdot \mathbf{s}_i \mathcal{P}_l^{\lambda}$$

$$\Delta U_l^{\lambda}(r) = U_{l,j=l+1/2}^{\lambda}(r) - U_{l,j=l-1/2}^{\lambda}(r)$$

- (a) P. Hafner, W. H. E. Schwarz, *Chem. Phys. Lett.* **65** (1979) 537;  
(b) P. A. Christiansen, Y. S. Lee, K. S. Pitzer, *J. Chem. Phys.* **71** (1979) 4445;  
(c) R. M. Pitzer, N. W. Winter, *J. Phys. Chem.* **92** (1988) 3061;  
A. Chang, R. M. Pitzer, *J. Am. Chem. Soc.* **111** (1989) 2500

## Recent reviews on ECPs for atoms and molecules

K. Balasubramanian, in: P. v. R. Schleyer et al. (eds.), *Encyclopedia of Computational Chemistry*, Vol. 4 (Q-S), Wiley, Chichester, UK, 1998, pp. 2471–2480

L. Seijo, Z. Barandiarán, in: J. Leszczynski (ed.), *Computational Chemistry, Reviews of Current Trends*, Vol. 4, World Scientific, Singapore, 1999, pp. 55–152

M. Dolg, in: J. Grotendorst (ed.), *Modern Methods and Algorithms of Quantum Chemistry (NIC Series, Vol. 1)*, John von Neumann Institute for Computing, Jülich, 2000, pp. 479–508 [ 2nd ed. (NIC Series, Vol. 3), pp. 507–540 ]

M. Dolg, in: P. Schwerdtfeger (ed.), *Relativistic Electronic Structure Theory, Part I: Fundamentals (Theoretical and Computational Chemistry, Vol. 11)*, Elsevier, Amsterdam, 2002, pp. 793–862

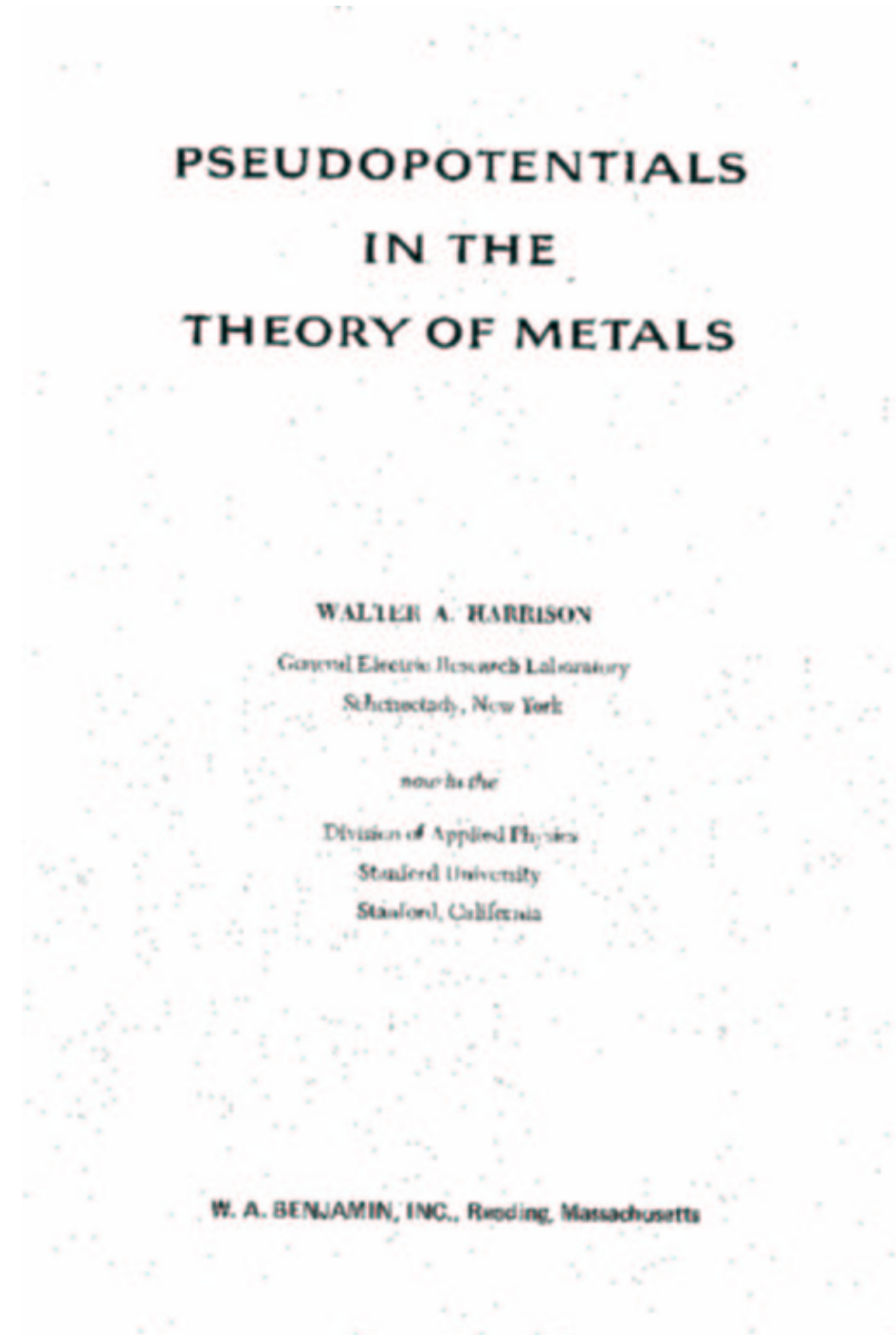
For earlier reviews see references given in the reviews above.

## Pseudopotentials in solid state science

W. A. Harrison, *Pseudopotentials in the Theory of Metals*, Benjamin, New York, 1966

based on the work by:

J. C. Phillips, L. Kleinman, *Phys. Rev.* **116** (1959) 287; M. H. Cohen, V. Heine, *Phys. Rev.* **122** (1961) 1821; V. Heine, I. V. Abarenkov, *Philos. Mag.* **9** (1964) 451 & **12** (1965) 529



Non-local pseudopotentials, designed to be used in plane-wave DFT calculations for periodic systems (crystals) – general form

$$U^\lambda = U_{\text{loc}}^\lambda + \sum_{ij} |\chi_i^\lambda\rangle B_{ij}^\lambda \langle \chi_j^\lambda| \quad \text{or} \quad U^\lambda = \sum_{ij} |\chi_i^\lambda\rangle B_{ij}^\lambda \langle \chi_j^\lambda|$$

The 'smoother' (or 'softer') the pseudopotential, the better (faster) the convergence of the plane wave expansions. The 'lack' of deep potential wells, due to introduction of the pseudopotential, was already recognized by **Hellmann** (see the German ed. of his book, Fig. 4, p. 39)

### Norm-conserving pseudopotentials:

- (a) D. R. Hamann, M. Schlüter, C. Chiang, *Phys. Rev. Lett.* **43** (1979) 1494
- (b) L. Kleinman, D. M. Bylander, *Phys. Rev. Lett.* **48** (1982) 1425
- (c) G. B. Bachelet, D. R. Hamann, M. Schlüter, *Phys. Rev. B* **26** (1982) 4199
- (d) D. Vanderbilt, *Phys. Rev. B* **32** (1985) 8412
- (e) N. Troullier, J. L. Martins, *Solid State Commun.* **74** (1990) 613
- (f) X. Gonze, R. Stumpf, M. Scheffler, *Phys. Rev. B* **44** (1991) 8503;  
M. Fuchs, M. Scheffler, *Comput. Phys. Commun.* **119** (1999) 67
- (g) S. Goedecker, M. Teter, J. Hutter, *Phys. Rev. B* **54** (1996) 1703;  
C. Hartwigsen, S. Goedecker, J. Hutter, *Phys. Rev. B* **58** (1998) 3641

### (Ultra)soft pseudopotentials:

D. Vanderbilt, *Phys. Rev. B* **41** (1990) 7892

see also PWScf, URL <http://www.pwscf.org>, for solid state DFT calcs. using plane wave basis, S. Baroni et al., Trieste, Italy

# Recent extensions of the ECP idea



## Effective group (or fragment) potentials (EGP / EFP)

Instead of 'replacing' only an atomic core by an effective one-electron operator (ECP), a fragment of the molecular system (an inactive group of atoms, or an inactive part of the electronic structure) is 'replaced' by an effective potential: the effective fragment (or group) potential

Some references (incomplete):

- (a) K. Ohta, Y. Yoshioka, K. Morokuma, K. Kitaura, *Chem. Phys. Lett.* **101** (1983) 12  
(effective fragment potential)
- (b) M. v. Arnim, S. D. Peyerimhoff, *Theor. Chim. Acta* **87** (1993) 41;  
M. v. Arnim, S. D. Peyerimhoff, *Chem. Phys. Lett.* **210** (1993) 488  
(effective potential for spectator groups)
- (c) J. A. M. Romero, J. F. Sanz, *J. Chem. Phys.* **99** (1993) 1255 (group model potential)
- (d) D. Andrae, Thesis, Univ. Stuttgart, 1994 (energy-consistent approach)
- (e) F. Alary, R. Poteau, J.-L. Heully, J.-C. Barthelat, J.-P. Daudey, *Theor. Chem. Acc.* **104** (2000) 174  
(effective group potentials)

## Embedding potentials

Instead of 'replacing' only an atomic core by an effective one-electron operator (ECP), the complete surrounding environment of a system (in a crystal) is 'replaced' by an effective potential: the embedding potential

→ see presentation given by L. Seijo

# Summary

## Effective core potentials (ECPs)

- a tool to study systems involving heavy atoms
- only a 'valence part' is treated explicitly ( $\neq$  the chemist's 'valence system')
- not (too) much loss of accuracy in valence properties
- most important relativistic effects (scalar relativistic effects) included in formally non-relativistic approaches
- not uniquely defined — many varieties exist