IL NUOVO CIMENTO VOL. 110 A, N. 9-10 Settembre-Ottobre 1997

Pseudopotentials for Clusters(*)

E. ENGEL, A. HÖCK, R. M. DREIZLER
Institut für Theoretische Physik, Universität Frankfurt, Robert-Mayer-Str. 8-10,
D-60054 Frankfurt/Main, Germany

(ricevuto il 28 Luglio 1997; approvato il 15 Ottobre 1997)

Summary. — The relativistic optimized-potential-method is used to generate norm-conserving pseudopotentials. First results for Sodium indicate that the resulting pseudopotentials are superior to those based on the local density approximation.

PACS 31.10 – Theories of electronic structure, electronic transitions, and chemical binding.
PACS 71.15.Hx – Pseudopotential method.
PACS 71.15.Mb – Density functional theory, local density approximation.
PACS 01.30.Cc – Conference proceedings.

1. – Introduction

The standard $ab - initio$ approach to electronic structure calculations for clusters combines two concepts:

- The ionic cores of the cluster constituents are described by pseudopotentials, thus eliminating all those degrees of freedom which are (hopefully) irrelevant for the molecular structure. The most extreme example of this concept is provided by the jellium model for metal clusters, in which all ionic cores are added up to form a single, structureless pseudopotential.
- Density functional (DF) methods are used for both the construction of the pseudopotentials and the actual molecular structure calculations.

In this contribution we present first results for pseudopotentials obtained with the most advanced DF technique available to date, i.e. the optimized-potential-method (OPM), in which orbital-dependent representations of the exchange-correlation (xc) energy functional are used. As the pseudopotential concept is particularly attractive for heavy elements we base our discussion on a relativistic variant of the OPM [1, 2, 3]. The OPM is

---

(*) Paper presented at the 174. WE-Heraeus-Seminar "New Ideas on Clustering in Nuclear and Atomic Physics", Rauischholzhausen (Germany), 9-13 July, 1997 combined with the often used pseudopotential scheme by Bachelet, Hamann and Schlüter [4]. First results for Sodium are compared with the standard pseudopotentials generated with the local density approximation (LDA).

2. – Relativistic optimized potential method (ROPM)

For the construction of pseudopotentials one relies on the density-only (electrostatic) variant [1, 2] of relativistic DF theory (DFT), in which the presence of external magnetic fields is excluded. In addition, the no-(virtual-)pair approximation is utilized, and, for brevity, the transverse (Breit) interaction is neglected (their inclusion, appropriate for very heavy elements, is straightforward — compare [3]). One can then represent the ground state density n in terms of auxiliary single particle spinors φ_k,

$$n(\boldsymbol{r}) = \sum_{-m<\epsilon_k\le\epsilon_F} \varphi_k^+(\boldsymbol{r})\varphi_k(\boldsymbol{r}) \ , \tag{1}$$

and decompose the total energy as ($\hbar = c = 1$)

$$E_{tot} = \sum_{-m<\epsilon_k\le\epsilon_F} \int d^3r \ \varphi_k^+(\boldsymbol{r})\big[-i\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta m + v_{ext}(\boldsymbol{r})\big]\varphi_k(\boldsymbol{r}) + E_H + E_{xc} \tag{2}$$

$$E_H = \frac{e^2}{2}\int d^3r \int d^3r' \ \frac{n(\boldsymbol{r})\ n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \ , \tag{3}$$

thereby defining the xc-energy functional E_{xc}. Minimization of E_{tot} with respect to the φ_k's leads to the relativistic Kohn-Sham equations,

$$\big\{-i\boldsymbol{\alpha}\cdot\boldsymbol{\nabla} + \beta m + v^{KS}([n];\boldsymbol{r})\big\}\varphi_k(\boldsymbol{r}) = \epsilon_k\varphi_k(\boldsymbol{r}) \tag{4}$$

$$v^{KS}([n];\boldsymbol{r}) = v_{ext}(\boldsymbol{r}) + e^2\int d^3r' \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} + \frac{\delta E_{xc}}{\delta n(\boldsymbol{r})} \ . \tag{5}$$

Via (2) all complex many-body effects have been absorbed into E_{xc}, for which a suitable approximation is now required. In standard DFT E_{xc} is approximated by an explicit functional of n, as for instance the LDA. In the (R)OPM E_{xc} is allowed to be orbital-dependent, thus only implicitly being a density functional. The most obvious orbital-dependent functional is the DF exchange, given by the relativistic Fock term,

$$E_x = -\frac{e^2}{2}\sum_{-m<\epsilon_k,\epsilon_l\le\epsilon_F}\int d^3r\int d^3r' \ \frac{\varphi_k^+(\boldsymbol{r})\varphi_l(\boldsymbol{r})\varphi_l^+(\boldsymbol{r}')\varphi_k(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|} \ . \tag{6}$$

Eq.(6) defines the exchange-only part of E_{xc}, the remainder representing the DF correlation energy E_c. E_c may also be orbital-dependent, as in the Colle-Salvetti functional [5]. The development of orbital-dependent E_c, however, is still at the beginning.

In the case of orbital-dependent E_{xc} the xc-potential $v_{xc}(\boldsymbol{r}) = \delta E_{xc}/\delta n(\boldsymbol{r})$, required for (5), can not be evaluated directly. In order to derive an equation which determines v_{xc} one replaces the functional derivative with respect to n by one with respect to φ_k,

$$\frac{\delta E_{xc}}{\delta n(\boldsymbol{r})} = \int d^3r' \ d^3r'' \sum_{-m<\epsilon_k\le\epsilon_F} \frac{\delta v^{KS}(\boldsymbol{r}')}{\delta n(\boldsymbol{r})}\frac{\delta\varphi_k^+(\boldsymbol{r}'')}{\delta v^{KS}(\boldsymbol{r}')}\frac{\delta E_{xc}}{\delta\varphi_k^+(\boldsymbol{r}'')} + c.c. \ . \tag{7}$$

TABLE I. – Selfconsistent, exchange-only ground state energies from ROPM, RHF, RLDA and RPW91 calculations for neutral atoms with closed subshells (transverse and radiative contributions neglected — all energies in *mhartree*).

Atom	E_{tot}	$E_{tot} - E_{tot}[ROPM]$		
	ROPM	RHF	RLDA	RPW91
He	-2862	0	138	6
Be	-14575	-1	350	18
Ne	-128690	-2	1062	-24
Ar	-528678	-5	2341	41
Ca	-679704	-6	2656	26
Zn	-1794598	-14	4140	-262
Kr	-2788848	-13	5565	-21
Xe	-7446876	-19	9800	85
Yb	-14067621	-48	13272	-893
Hg	-19648826	-39	17204	-250

Insertion of the linear response of φ_k to a small variation of v^{KS}, multiplication of (7) with the static Kohn-Sham response function $\delta n(\boldsymbol{r}''')/\delta v^{KS}(\boldsymbol{r})$ and subsequent integration over $\boldsymbol{r}$ leads to the ROPM integral equation,

$$\int d^3r' \; \chi^{KS}(\boldsymbol{r},\boldsymbol{r}') \; v_{xc}(\boldsymbol{r}') \;=\; Q_{xc}(\boldsymbol{r}) \;, \tag{8}$$

where

$$\chi^{KS}(\boldsymbol{r},\boldsymbol{r}') = \sum_{-m<\epsilon_k\le\epsilon_F<\epsilon_l} \frac{\varphi_k^{+}(\boldsymbol{r})\varphi_l(\boldsymbol{r})\varphi_l^{+}(\boldsymbol{r}')\varphi_k(\boldsymbol{r}')}{\epsilon_k-\epsilon_l} + \; c.c. \;=\; \frac{\delta n(\boldsymbol{r})}{\delta v^{KS}(\boldsymbol{r}')} \tag{9}$$

$$Q_{xc}(\boldsymbol{r}) = \sum_{-m<\epsilon_k\le\epsilon_F} \int d^3r' \; \varphi_k^{+}(\boldsymbol{r}) \sum_{l\neq k} \frac{\varphi_l(\boldsymbol{r}) \; \varphi_l^{+}(\boldsymbol{r}')}{\epsilon_k-\epsilon_l} \frac{\delta E_{xc}}{\delta\varphi_k^{+}(\boldsymbol{r}')} \; + \; c.c. \;. \tag{10}$$

Eq.(8) has to be solved selfconsistently together with the single particle equations (4). By construction the combination $E_H + E_x$ is self-interaction free, which is reflected by the asymptotic behavior of the exchange potential for finite systems, $v_x(|\boldsymbol{r}| \to \infty) \sim -1/|\boldsymbol{r}|$.

If one neglects E_c completely one arrives at the DF equivalent of the relativistic Hartree-Fock (RHF) approximation. In order to demonstrate the advantage of orbital-dependent E_{xc} as compared with actual density functionals it is thus useful to restrict the discussion to the exchange-only limit, where RHF-results can serve as reference standard from a physical point of view. The corresponding ROPM and RHF ground state energies E_{tot} for some neutral atoms with closed subshells are given in Table I together with results obtained with the relativistic LDA (RLDA) [2] and a relativistic extension (RPW91) [3] of the Perdew-Wang generalized gradient approximation (GGA) [6]. Table I shows that the ROPM energies are very close to the RHF values, the differences being below $50 mhartree$. In fact, this is not only true for E_{tot}, but also for the more interesting quantities as ionization potentials etc, thus demonstrating that the exchange-only ROPM is physically equivalent to the RHF-approximation. This clearly supports the DF-concept of a local xc-potential. On the other hand, the error of the RLDA is substantial throughout the periodic system. RPW91 leads to errors which vary between 0.01 and $1.0 hartree$ in size

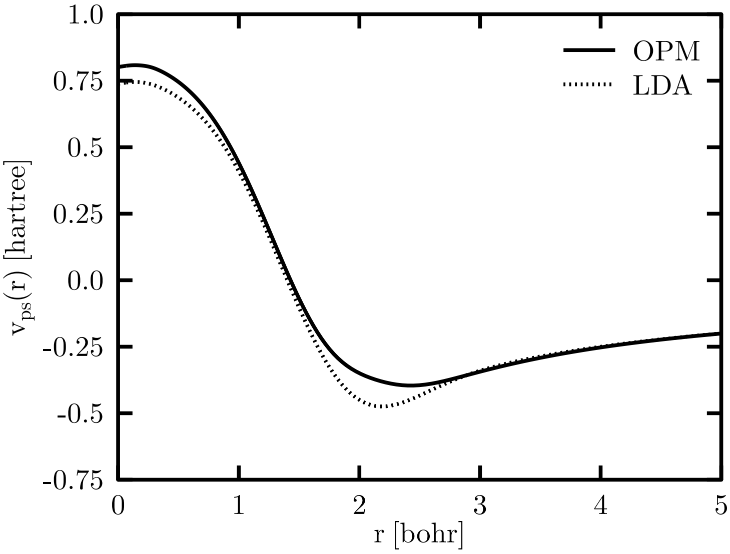

Fig. 1. – The *s*-pseudopotentials obtained from the combination of exact exchange with LDA correlation (OPM) as well as from the LDA for exchange and correlation (LDA).

and also in their sign. This indicates that error cancellation plays an important role. As a consequence one finds that more subtle quantities like ionization potentials are only marginally improved by the (R)PW91-GGA as compared with the (R)LDA [6].

3. – Normconserving pseudopotentials

For this first study we have closely followed the widely used scheme for the construction of normconserving pseudopotentials by Bachelet, Hamann and Schlüter [4], which is briefly reviewed in the following. For each valence level of interest (characterized by its angular momentum quantum numbers lj) one starts with an all-electron calculation for a suitably chosen configuration ν: For levels occupied in the atomic ground state the ground state configuration is used, while for levels unoccupied in the ground state an excited state configuration (with fractional occupancy) is utilized. This yields a total all-electron Kohn-Sham potential $v^{KS,\nu}(r)$, Eq.(5), as well as the corresponding radial orbitals $a^{\nu}_{nlj}(r)$ (only the properly normalized large components are relevant here) and eigenvalues ϵ^{ν}_{nlj} (in the case of open shells a spherical average is used). One then constructs a first level pseudopotential $v^{(1)\nu}_{ps,lj}$, using a switching function f,

$$(11) \qquad v^{(1)\nu}_{ps,lj}(r) = A_{lj} f(r/r^c_{lj}) + [1 - f(r/r^c_{lj})] v^{KS,\nu}(r) \qquad ; \qquad f(x) = \exp(-x^{\lambda}) \ ,$$

so that the eigenvalue of the corresponding lowest occupied (i.e. nodeless) pseudoorbital $w^{(1)\nu}_{lj}$ agrees with its all-electron counterpart (in this way determining A_{lj} — the ν-dependence of all constants is suppressed for brevity). For both the switching range (λ) and radius (r^c_{lj}) we have chosen the values of Ref.[4], i.e. $\lambda = 3.5$ and r^c_{lj} is evaluated from the outermost extremum of a^{ν}_{nlj} via Table I of [4]. As for $r > r^c_{lj}$ $v^{(1)\nu}_{ps,lj}(r)$ is identical with $v^{KS,\nu}(r)$ (up to exponentially small corrections), one essentially has $w^{(1)\nu}_{lj}(r) =$

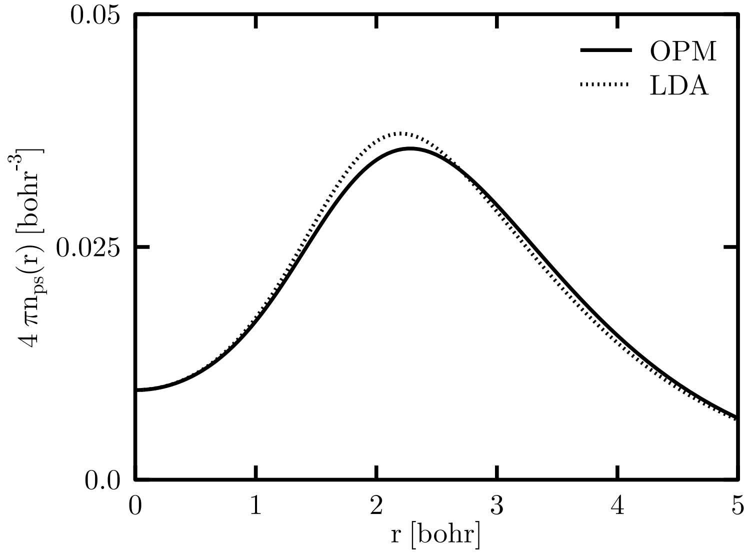

Fig. 2. – Pseudoorbitals ($4\pi r^2 n_{ps} = [w^{\nu}_{lj}(r)]^2$) corresponding to the potentials in Fig.1.

const × $a^{\nu}_{nlj}(r)$ in this regime. In the next step $w^{(1)\nu}_{lj}$ thus is scaled by a constant,

$$w^{\nu}_{lj}(r) = B_{lj}\left[w^{(1)\nu}_{lj}(r) + C_{lj} r^{l+1} f(r/r^c_{lj})\right] \ , \tag{12}$$

so that $w^{\nu}_{lj}(r) = a^{\nu}_{nlj}(r)$ for $r > r^c_{lj}$. C_{lj} ensures proper normalization, its r^{l+1} prefactor the required behavior for small r. The potential $v^{(2)\nu}_{ps,lj}$ which leads to w^{ν}_{lj} is given by [4]

$$\begin{aligned} v^{(2)\nu}_{ps,lj}(r) = {} & v^{(1)\nu}_{ps,lj}(r) + B_{lj} C_{lj} \frac{r^{l+1} f(r/r^c_{lj})}{w^{\nu}_{lj}(r)} \\ & \times \left\{ \frac{\lambda^2 (r/r^c_{lj})^{2\lambda} - [2\lambda l + \lambda(\lambda+1)](r/r^c_{lj})^{\lambda}}{2r^2} + \epsilon^{\nu}_{nlj} - v^{(1)\nu}_{ps,lj}(r) \right\} \ . \end{aligned} \tag{13}$$

Finally, $v^{(2)\nu}_{ps,lj}$ is unscreened, i.e. the interaction among the occupied valence levels (and their spurious self-interaction, if present) is eliminated,

$$v^{\nu}_{ps,lj}(r) = v^{(2)\nu}_{ps,lj}(r) - \int d^3r' \, \frac{n^{\nu}_{ps}(r')}{|\boldsymbol{r} - \boldsymbol{r}'|} - v_{xc}([n^{\nu}_{ps}]; r) \tag{14}$$

$$n^{\nu}_{ps}(r) = \sum_{occ.val.orb.} f^{\nu}_{lj} \, \frac{w^{\nu}_{lj}(r)^2}{4\pi r^2} \ . \tag{15}$$

For the calculation of angular momenta corresponding to excited single particle states of a given atom the occupation factors f^{ν}_{lj} have been chosen according to Table II of Ref.[4].

The procedure (11-15) has originally been introduced on the basis of the LDA. However, all steps involved can also be taken for orbital-dependent xc-functionals. As in the case of the LDA [4], the unscreening (14) implies a 'linearization' of the orbital-dependent E_{xc} as far as the valence-core interaction is concerned (however, nonlinear core-corrections may also be included for orbital-dependent E_{xc}).

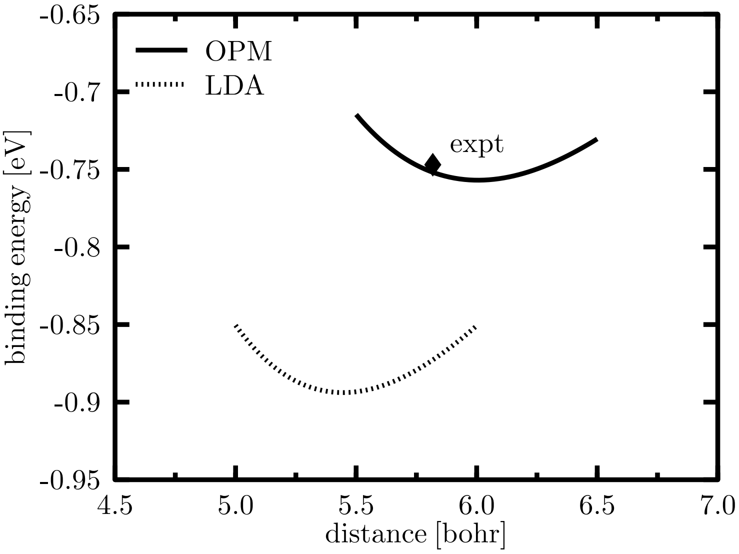

Fig. 3. – Energy surfaces of the Sodium-dimer obtained with OPM- and LDA pseudopotentials.

4. – Results for Sodium

For this exploratory study of ROPM-pseudopotentials we have combined the exact exchange (6) with the LDA for correlation (in the form of Ref.[7]). The result for the $s(l = 0)$-pseudopotential of Na is compared with its LDA counterpart in Fig.1. The corresponding s-pseudoorbitals are shown in Fig.2. As is obvious from these Figures, the ROPM-pseudoorbital is somewhat less localized than the LDA-orbital, reflecting the more shallow ROPM-pseudopotential.

As a first application of the ROPM-pseudopotentials we have considered the Na-dimer, including s, p and d-contributions and using the d-potential as local potential (for $l \neq 0$ we have combined the two relevant $v^{\nu}_{ps,lj}$ according to their statistical weight, $v^{\nu}_{ps,l} = [2l v^{\nu}_{ps,l,l-1/2} + (2l+2) v^{\nu}_{ps,l,l+1/2}]/(4l+2)$ — the technical details of the two-center calculation are as in Ref.[8]). In order to isolate the effect of the pseudopotentials we have used the LDA for the complete $E_{xc}[n]$ in the molecular calculations for both the OPM- and the LDA-pseudopotentials. Note that this does not introduce an inconsistency in the case of the OPM-pseudopotential as the interaction between the valence electrons is taken out of the pseudopotentials by the unscreening procedure (14) (in which, of course, the same functional has to be applied as in the all-electron calculation). The resulting energy surfaces are shown in Fig.3 in comparison with the experimental binding energy and equilibrium distance [9]. It is obvious that the results obtained with the OPM-pseudopotentials are much closer to the experimental situation than the LDA-predictions.

In fact, this close agreement with experiment suggests that the nonlocality of the all-electron xc-potential, responsible for the large deviations of the LDA-energies in Table I, has been absorbed into the ROPM-pseudopotentials to a large degree. Thus, while in general one would expect even more accurate results if the OPM is also used in the molecular calculation, at least for Na the much more efficient molecular LDA-calculation seems to be sufficient, making the ROPM-pseudopotentials particularly attractive.

* * *

REFERENCES

[1] ENGEL E., KELLER S., FACCO BONETTI A., MÜLLER H. AND DREIZLER R. M., *Phys. Rev. A*, **52** (1995) 2750.

[2] ENGEL E. AND DREIZLER R. M., *Top. Curr. Chem.*, **181** (1996) 1.

[3] ENGEL E., KELLER S. AND DREIZLER R. M., in *Electronic Density Functional Theory: Recent Progress and New Directions*, ed. by J. F. Dobson, G. Vignale and M. P. Das (Plenum, New York, 1997).

[4] BACHELET G. B., HAMANN D. R. AND SCHLÜTER M., *Phys. Rev. B*, **26** (1982) 4199.

[5] COLLE R. AND SALVETTI O., *Theoret. Chim. Acta (Berl.)*, **37** (1975) 329.

[6] PERDEW J. P., CHEVARY J. A., VOSKO S. H., JACKSON K. A., PEDERSON M. R., SINGH D. J. AND FIOLHAIS C., *Phys. Rev. B*, **46** (1992) 6671.

[7] VOSKO S. H., WILK L. AND NUSAIR M., *Can. J. Phys.*, **58** (1980) 1200.

[8] ENGEL E., SCHMITT U. R., LÜDDE H.-J., TOEPFER A., WÜST E., DREIZLER R. M., KNOSPE O., SCHMIDT R. AND CHATTOPADHYAY P., *Phys. Rev. B*, **48** (1993) 1862.

[9] VERMA K. K., BAHNS J. T., REJEI-RIZI A. R., STWALLEY W. C. AND ZEMKE W. T., *J. Chem. Phys.*, **78** (1983) 3599.