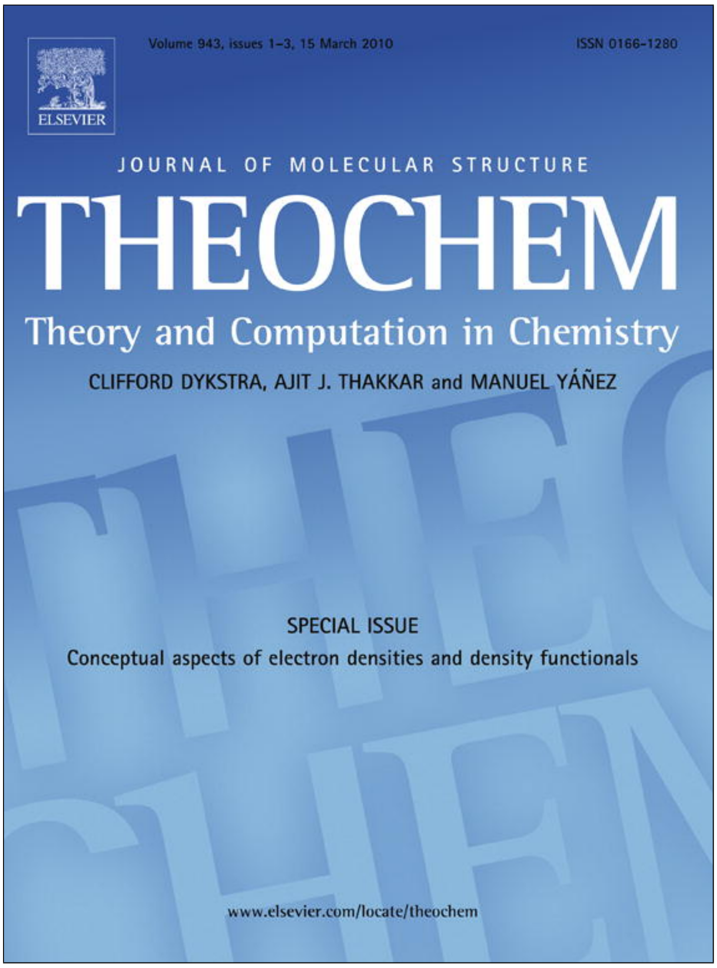

Volume 943, issues 1–3, 15 March 2010

ISSN 0166-1280

ELSEVIER

JOURNAL OF MOLECULAR STRUCTURE
THEOCHEM
Theory and Computation in Chemistry
CLIFFORD DYKSTRA, AJIT J. THAKKAR and MANUEL YÁÑEZ

SPECIAL ISSUE
Conceptual aspects of electron densities and density functionals

www.elsevier.com/locate/theochem

Journal of Molecular Structure: THEOCHEM 943 (2010) 90–93

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

Full configuration interaction wave function as a formal solution to the optimized effective potential and Kohn–Sham models in finite basis sets

Daniel R. Rohr [a], Andreas Savin [b,*]

[a] *Institute of Physics, Technical University Łódź, Wólczańska 219, 93-005 Łódź, Poland*
[b] *Laboratoire de Chemie Théorique, UMR 7616, CNRS and UMPC, Univ. Paris VI, 4, place Jussieu, F-75252 Paris Cedex 5, France*

ARTICLE INFO

Article history:
Received 26 August 2009
Received in revised form 29 October 2009
Accepted 30 October 2009
Available online 5 November 2009

Keywords:
Optimized effective potential
Density functional theory
Kohn–Sham
Full configuration interaction

ABSTRACT

Using *finite* basis sets, it is shown how to construct a local Hamiltonian, such that one of its infinitely many degenerate eigenfunctions is the ground-state full configuration interaction (FCI) wave function in that basis set. Formally, the local potential of this Hamiltonian is the optimized effective potential and the exact Kohn–Sham potential at the same time, because the FCI wave function yields the exact ground-state density and energy. It is not the aim of this paper to provide a new algorithm for obtaining FCI wave functions. A new potential is the goal.

1. Introduction

In the Kohn–Sham model (KS) [1,2], one considers a system of non-interacting fermions having the same ground-state density, $\rho(r)$, as a given system of interacting electrons. This is made possible by a convenient choice of the potential, $v_{\mathrm{KS}}(r)$, in which the non-interacting fermions move.

One can consider a model system of non-interacting fermions such that its ground-state wave function minimizes the expectation value of the Hamiltonian of a physical system of interacting electrons [3,4]. The potential describing this model system is the optimized effective potential, $v_{\mathrm{OEP}}(r)$, and this also gives the name to the method (OEP). The OEP method has recently been applied to minimize energy expressions in the framework of KS. In this paper, however, we understand OEP exclusively as a method to minimize the expectation value of a physical Hamiltonian.

With similar arguments like in Refs. [5–7] we construct a local potential for a *finite* orbital basis, such that all orbital energies are degenerate. This allows us to choose the full configuration interaction (FCI) wave function as the ground-state wave function. Thus, we obtain simultaneously the FCI density and energy. This means that the KS (exact density) and OEP (minimal energy) conditions can be satisfied within the given basis set.

In this paper we point out that the FCI wave function is the ground-state wave function of the local Hamiltonian constructed in this article if a *finite* basis set is employed. We are only interested in the potential. We do not suggest a new algorithm to obtain the FCI wave function.

In Section 2 we describe how to construct a fully degenerate non-local Hamiltonian. This is a non-local Hamiltonian with all orbitals degenerate. Furthermore, we show that in a *finite* basis a fully degenerate local Hamiltonian can be constructed from the fully degenerate non-local Hamiltonian. In Section 3 we analyze the conditions that must be satisfied to construct a fully degenerate local Hamiltonian. In Section 4 we give numerical examples for a fully degenerate local Hamiltonian. Section 5 discusses the consequences of a fully degenerate local Hamiltonian. We argue that the FCI wave function is a ground-state of the local Hamiltonian. In Section 6 we draw the conclusions.

2. Fully degenerate Hamiltonians

In this section we show, for a *finite* basis set, how to construct a local Hamiltonian that yields exactly the same orbitals and orbital energies as a given non-local Hamiltonian. The non-local Hamiltonian is fully degenerate, i.e. the orbitals are all degenerate.

Assume a system with N electrons and a *finite* basis set with M functions. We now search for a potential which makes all orbitals degenerate. Let us start with a local potential, $v(r)$. This can be the nuclear potential, $v_{nuc}(r)$ or this could be the KS or OEP potential, which include the nuclear potential. We obtain $\phi_m(r)$, the eigenfunctions of the non-interacting one-particle Hamiltonian

$$h_0 = -\frac{1}{2}\nabla^2 + v(r) \tag{1}$$

---

[*] Corresponding author.
E-mail addresses: rohrdr@gmail.com (D.R. Rohr), andreas.savin@lct.jussieu.fr (A. Savin).

0166-1280/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2009.10.037

The eigenvalues are ε_m. We add a non-local potential

$$v_{NL} = \sum_m^M |\phi_m\rangle(\varepsilon - \varepsilon_m)\langle\phi_m| \tag{2}$$

The eigenfunctions of the Hamiltonian

$$h_{NL} = -\frac{1}{2}\nabla^2 + v(r) + v_{NL} \tag{3}$$

remain $\phi_m(r)$, and they are all degenerate. Hence, it is possible to construct a Hamiltonian with a non-local potential that yields the same orbital energy for all orbitals.

Furthermore, in a *finite* basis set, we can construct a local potential, $v_L(r)$, such that

$$\langle\phi_m|v_L|\phi_n\rangle = \langle\phi_m|v + v_{NL}|\phi_n\rangle, \quad \forall m, n \tag{4}$$

Thus,

$$h_L = -\frac{1}{2}\nabla^2 + v_L(r) \tag{5}$$

produces the same (finite) Hamiltonian matrix as h_{NL}, and has all eigenvalues degenerate. Of course, the eigenstates of

$$H_{NL} = \sum_i^N h_{NL}(i) \tag{6}$$

and

$$H_L = \sum_i^N h_L(i) \tag{7}$$

are also degenerate, since they are made of all the determinants constructed from the ϕ_m. Thus, the ground-state FCI wave function in the space spanned by the ϕ_m is also an eigenstate of both H_{NL} and H_L. As usual the eigenvalue of H_L has no physical meaning.

3. Conditions for a fully degenerate local Hamiltonian

In the previous section we showed how to construct a fully degenerate local Hamiltonian, i.e. a local Hamiltonian with all orbitals degenerate. In this section we analyze the conditions that have to be met to insure that such a local Hamiltonian can be constructed.

To obtain eigenvalues that are all degenerate it is necessary to satisfy all of Eq. (4). In practice this can done by introducing a basis for the potential with, say K, functions.

$$v_L(r) = v(r) + \sum_t^K b_t g_t(r) \tag{8}$$

For convenience we separated $v_L(r)$ in $v(r)$, the local potential of Eq. (1), and expanded only the non-local rest in $\{g_t(r)\}$, the basis for the potential. Inserting this equation in the conditions (4) we obtain a set of equations

$$\sum_t^K b_t \int \phi_k(r)\phi_l(r)g_t(r)dr = \delta_{kl}(\varepsilon - \varepsilon_k) \quad ,\forall k \leqslant l \tag{9}$$

for which solutions can be sought for b_t.

This is possible when Eq. (9) are consistent. However, linear dependencies in the products of orbitals can produce inconsistencies. Let us, thus, assume the linear dependence

$$\phi_m(r)\phi_n(r) = \sum_{\substack{k\leqslant l\\ kl\neq mn}} c_{kl,mn}\phi_k(r)\phi_l(r) \tag{10}$$

We multiply each condition $kl \neq mn$ from (9) with the respective coefficient and sum them up. We obtain

$$\sum_t^K b_t \int \sum_{\substack{k\leqslant l\\ kl\neq mn}} c_{kl,mn}\phi_k(r)\phi_l(r)g_t(r)dr = \delta_{kl} \sum_{\substack{k\leqslant l\\ kl\neq mn}} c_{kl,mn}(\varepsilon - \varepsilon_k) \tag{11}$$

We have now used all conditions of Eq. (9) but the one for the pair mn. We subtract the remaining condition to obtain

$$\sum_t^K b_t \int \left(\sum_{\substack{k\leqslant l\\ kl\neq mn}} c_{kl,mn}\phi_k(r)\phi_l(r) - \phi_m(r)\phi_n(r) \right) g_t(r)dr$$
$$= \delta_{kl}\left(\sum_{\substack{k\leqslant l\\ kl\neq mn}} c_{kl,mn}(\varepsilon - \varepsilon_k) \right) - \delta_{mn}(\varepsilon - \varepsilon_m) \tag{12}$$

Now we use the assumed linear dependency (cf. (10)) to obtain

$$0 = \delta_{kl}\left(\sum_{\substack{k\leqslant l\\ kl\neq mn}} c_{kl,mn}(\varepsilon - \varepsilon_k) \right) - \delta_{mn}(\varepsilon - \varepsilon_m) \tag{13}$$

If we assume for a moment, that none of the products $\phi_i\phi_i$ are involved in the linear dependency of Eq. (10), the final equation (13) is trivially satisfied. In this case $m \neq n$ and $c_{kl,mn} = 0, \forall k = l$, and hence the right-hand side is equal to zero.

If only one product $\phi_i\phi_i$ is linearly dependent we obtain $0 = \varepsilon_i - \varepsilon$. This equation can be satisfied by choosing $\varepsilon = \varepsilon_i$. However, if more than one product $\phi_i\phi_i$ is linearly dependent on the rest of all orbital products, Eq. (13) cannot be satisfied.

In this section we found that the diagonal terms $\phi_i\phi_i$ must be linearly independent from the rest of all orbital products to guarantee a fully degenerate local Hamiltonian.

4. Numerical example

In this section we present numerical examples for a fully degenerate, *finite* basis, local Hamiltonian, i.e. a local Hamiltonian with all orbitals (finite number) degenerate. We consider He together with cc-pVDZ, cc-pVTZ and cc-pVQZ as an orbital basis, $\{\chi_i\}$, where we removed d- and f-functions. For the potential basis, $\{g_t\}$, we choose an even tempered basis of s-type gaussian orbitals with exponents ranging from 0.1 to 40 000. For the cc-pVDZ orbital basis we use 5 potential basis functions, for the cc-pVTZ we use 10 potential basis functions and for cc-pVQZ we use 25 potential basis functions. We use more potential basis functions than needed to insure that the space spanned by the orbital products is covered by our potential basis. The singular value decomposition used in our implementation will pick out only the necessary potential functions.

The goal is to construct a Hamiltonian matrix, which has all eigenvalues equal, i.e. there is an orbital basis, in which it is equal to some ε times the unit matrix. We choose $\varepsilon = 1$ for convenience. In a first step we calculate the one-electron matrix, $\mathbf{T}$, and the potential matrices, $\mathbf{G}_t$, in the orbital basis.

$$T_{ij} = \left\langle \chi_i \middle| -\frac{1}{2}\nabla^2 - \frac{2}{r} \middle| \chi_j \right\rangle \tag{14}$$

$$G_{t,ij} = \langle\chi_i|g_t|\chi_j\rangle \tag{15}$$

The goal is to find a set of b_t, such that

$$\mathbf{I} = \mathbf{T} + \sum_t^K b_t \cdot \mathbf{G}_t \tag{16}$$

holds, where $\mathbf{I}$ is the unit matrix. Collecting the matrices $\mathbf{G}_t$ in a super matrix $\mathbf{G}$, where the $\mathbf{G_t}$ form the tth column and rearranging Eq. (16) yields as a solution

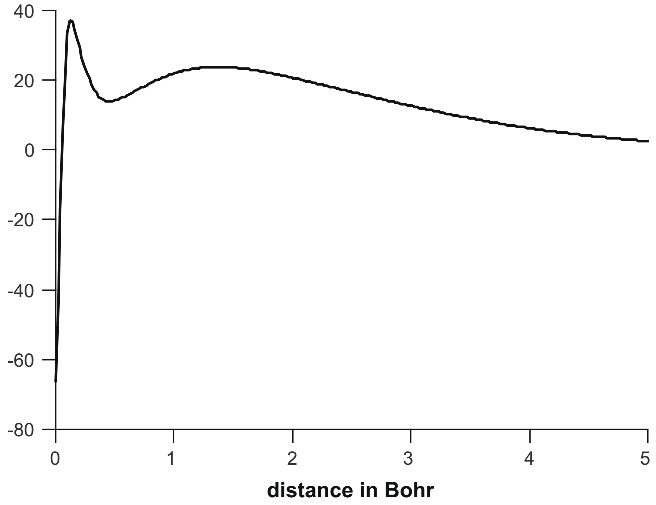

Fig. 1. The displayed potential is the local potential minus the nuclear potential, $v_L(r) - v_{nuc}(r)$ (for the potential basis see text). It yields the unit matrix in the cc-pvdz orbital basis.

$$\mathbf{b} = (\mathbf{I} - \mathbf{T}) \cdot \mathbf{G}^{-1} \tag{17}$$

Since the matrix **G** is, in general, not square but rectangular, we use a singular value decomposition to calculate the pseudo-inverse $\mathbf{G}^{-1}$.

With the cc-pVDZ orbital basis we are able to obtain the unit matrix with an accuracy of 10^{-14}. For the cc-pVTZ orbital basis the accuracy is 10^{-11} and for cc-pVQZ the accuracy is 10^{-7}. Figs. 1–3 display the expanded part of the potentials (cf. Eq. (8)) that yield the unit matrix in the given orbital basis. Strong oscillations are found close to the nucleus, as was reported in similar calculations [5,6]. In comparison we also show a very accurate KS potential in Fig. 4 [8].

When comparing the corrections to the electron–nucleus potential we notice that v_L having the FCI wave function as a solution (Figs. 1–3) is quite different from the accurate KS one (Fig. 4). Not only the shape largely differs, but also the order of magnitude (Please notice the change of scale between figures.) Furthermore, no convergence towards the correct KS potential can be seen.

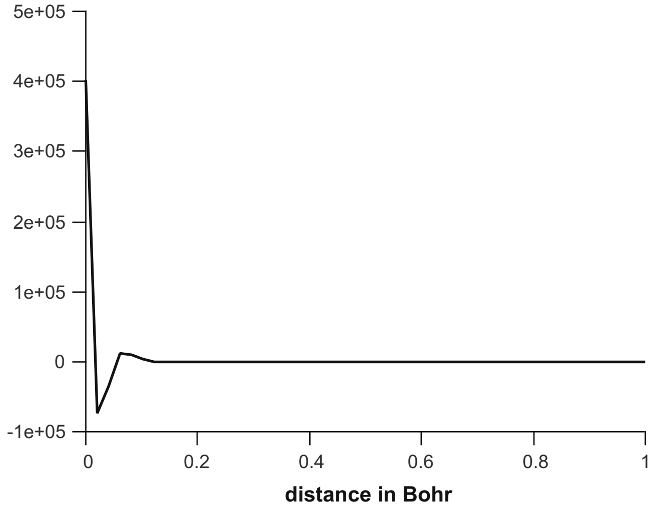

Fig. 2. The displayed potential is the local potential minus the nuclear potential, $v_L(r) - v_{nuc}(r)$ (for the potential basis see text). It yields the unit matrix in the cc-pvtz orbital basis.

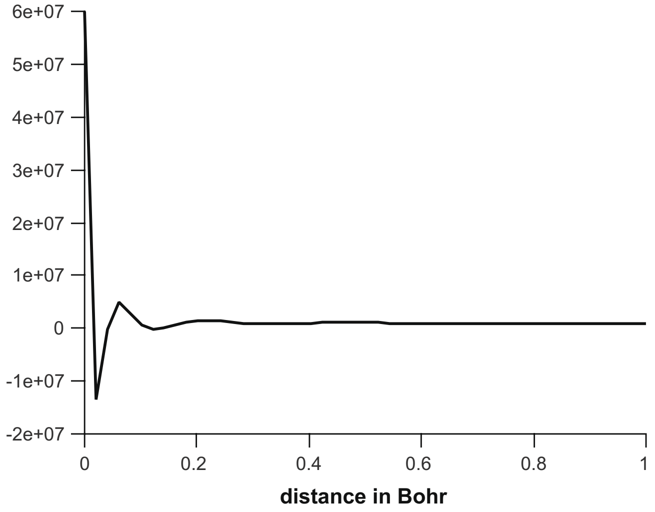

Fig. 3. The displayed potential is the local potential minus the nuclear potential, $v_L(r) - v_{nuc}(r)$ (for the potential basis see text). It yields the unit matrix in the cc-pvqz orbital basis.

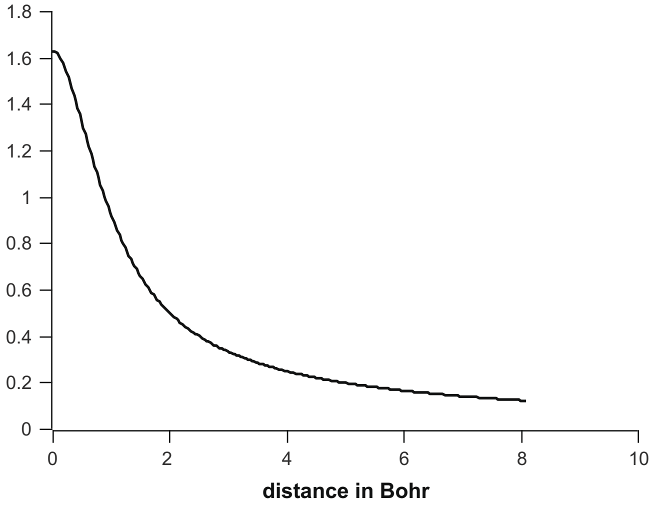

Fig. 4. A very accurate KS potential for He minus the nuclear potential.

5. Discussion

In this paper we want to obtain the OEP and KS potential for He in a given *finite* basis set. The KS potential is that potential that yields the FCI density [2]. In this respect the FCI density must be known to determine the KS potential. The OEP potential, on the other hand, is that potential whose ground-state wave function minimizes the expectation value of the physical Hamiltonian [3].

In general, $v_{\mathrm{KS}}(r)$ and $v_{\mathrm{OEP}}(r)$ are not identical. It is well known, that the OEP potential of helium, for a complete basis, is the Hartree potential. At the same time it is clear that the KS potential must differ, since the Hartree potential does not yield the exact density.

Both, for the KS and the OEP models, there is no interaction between fermions and thus, in general, the ground-state of the system can be described by a single Slater determinant. In the case of degeneracy of two or more single Slater determinants, any linear combination of the degenerate single Slater determinants is also a ground-state.

In the previous sections we showed how to construct a fully degenerate local Hamiltonian for a *finite* basis set. As a consequence, each and every wave function is a ground-state of the local Hamiltonian. The OEP procedure demands to pick that wave function that minimizes the expectation value of the physical Hamiltonian. Doubtless, this must be the FCI wave function.

There is no wave function that yields a lower energy than the FCI wave function. Consequently, the potential constructed in the previous sections is the OEP potential in the given *finite* basis set. At the same time this potential yields the FCI density. Consequently, the potential is also the KS potential.

The potential that we constructed is not unique. It will differ if a different potential basis $g_t(r)$ will be used. The choice of ε, the energy at which all orbitals are degenerate, will also influence the potential. Finally, the exact density can also be obtained from the local potential of a Schrödinger-like equation for $\sqrt{\rho(r)}$ [10].

To obtain the OEP or KS wave function it does not suffice to solve Eq. (17) and diagonalize the corresponding local Hamiltonian. More effort is needed. The FCI wave function must be constructed in the usual way [11,12].

6. Conclusion

In the optimized effective potential (OEP) and the Kohn–Sham (KS) models one usually tries to avoid degeneracies. In this paper, however, we focus on the consequences of degeneracies. In an approach similar to the ones taken in Refs. [5,6] we construct a fully degenerate local Hamiltonian. This means that all orbitals have the same energy.

The independent particle Hamiltonian constructed with $v_L(r)$ (cf. Eq. (5)) simultaneously yields the ground-state density for this basis set (the FCI density) and the lowest possible expectation value of the physical, interacting Hamiltonian (the FCI energy). Thus, the model Hamiltonian corresponds to both the KS and OEP solutions. Consequently, we have constructed a KS and OEP potential at the same time. We did not construct the FCI wave function, which may be obtained from standard procedures [11,12].

We believe that the conditions outlined in Section 3 can not be satisfied with very large basis sets. In Section 4 we see already for the cc-pVQZ basis a deviation of 10^{-7}. We conjecture, that Eq. (9) cannot be satisfied, when the size of the basis set increases, due to the over-completeness of the orbital products basis. This has also been noticed when attempting to construct the density matrix from the density [7,9].

Acknowledgments

Stimulating discussions with Drs. Paola Gori Giorgi (CNRS, Paris, France), Francois Colonna (CNRS, Paris, France) and Julien Toulouse (UPMC, Univ Paris 6, Paris, France) are gratefully acknowledged. We also thank C. Umrigar (Cornell University, Ithaca, USA) for providing us the Kohn–Sham potential of He.

One of the authors (AS) gratefully remembers an early discussion when his PhD adviser, Prof. H. Preuss, told him that in the sixties there were people who did not believe that the Hohenberg–Kohn theorem was correct, because one could construct the potentials the way pseudopotentials were constructed. One could fit as many parameters as desired to obtain the density to a given resolution. As for pseudopotentials, the Ansatz for the construction of the potential was considered arbitrary, and thus the potential determining the density was supposed to be not unique.

One of the authors (AS) gratefully acknowledges financial support from the ANR under grant number WADEMECOM (ANR-07-BLAN-0271).

One of the authors (DR) gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft under grant number RO 3894/1-1.

References

[1] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B 864.
[2] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A 1133.
[3] R.T. Sharp, G.K. Horton, Phys. Rev. 90 (1953) 317.
[4] J.D. Talman, W.F. Shadwick, Phys. Rev. A 14 (1976) 36.
[5] V.N. Staroverov, G.E. Scuseria, E.R. Davidson, J. Chem. Phys. 124 (2006) 141103.
[6] D.R. Rohr, O. Gritsenko, E.J. Baerends, Chem. Phys. Lett. 432 (2006) 336.
[7] J.E. Harriman, Phys. Rev. A 27 (1983) 632.
[8] C. Umrigar, X. Gonze, Phys. Rev. A 50 (1994) 3827.
[9] W.H.E. Schwarz, B. Müller, Chem. Phys. Lett. 166 (1990) 621.
[10] R. Dreizler, E.K.U. Gross, Density Functional Theory, Springer-Verlag, Berlin, 1990.
[11] P.J. Knowles, N.C. Handy, Chem. Phys. Lett. 111 (1984) 315.
[12] P.J. Knowles, N.C. Handy, Comp. Phys. Commun. 54 (1989) 75.