



A new quasi-relativistic approach for density functional theory based on the normalized elimination of the small component

Michael Filatov, Dieter Cremer *

Department of Theoretical Chemistry, University of Göteborg, Reutersgatan 2, Göteborg S-41320, Sweden

Received 26 October 2001

Abstract

A recently developed variationally stable quasi-relativistic method, which is based on the low-order approximation to the method of normalized elimination of the small component, was incorporated into density functional theory (DFT). The new method was tested for diatomic molecules involving Ag, Cd, Au, and Hg by calculating equilibrium bond lengths, vibrational frequencies, and dissociation energies. The method is easy to implement into standard quantum chemical programs and leads to accurate results for the benchmark systems studied. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Density functional theory (DFT) [1,2] is a widely used tool in computational chemistry to study the properties of atoms and molecules. For electronic systems containing heavy atoms relativistic effects have to be taken into consideration to obtain accurate results [3,4]. For this purpose, DFT was extended to the relativistic domain [5,6]. However, relativistic DFT based on the Dirac–Hartree–Fock approach implies a four-component formalism, which makes computations much more expensive than for non-relativistic DFT.

Since the full four-component formalism is computationally demanding, many efforts have been made to obtain a two-component formalism

or even, by removing the spin-degrees of freedom, a one-component form [7–13]. As a price for the reduction of the four-component formalism, non-linear energy-dependent operators appear in the two-component relativistic Hamiltonian. It is a common way to remove the energy dependence of the Hamiltonian by expansion of the non-linear operators in terms of powers of $1/c^2$ [8–11] and to obtain approximate quasi-relativistic approaches. The latter rely often on sophisticated transformations and require the use of molecular integrals which otherwise would not appear in conventional DFT calculations [8–11]. Hence, quasi-relativistic DFT methods are difficult to implement into standard DFT programs. Computationally, they are more demanding than Kohn–Sham DFT [1].

Furthermore, the approximations invoked into some quasi-relativistic DFT schemes can result in a loss of gauge invariance and in the non-stationarity of the energy, like in the zeroth-order regular ap-

* Corresponding author. Fax: +46-31-773-5590.

E-mail address: cremer@theoc.gu.se (D. Cremer).

proximation (ZORA) [10,11], or in a loss of variational stability, like in the relativistic elimination of the small component (RESC) approach [14]. In the case of the ZORA approach, additional approximations have to be made to restore its gauge invariance and the stationarity of the energy [10,11,15]. The RESC method must be used with contracted basis sets which do not contain basis functions with very high exponents to avoid a variational collapse [14]. This makes the RESC method inconvenient for the calculation of the properties which depend strongly on the completeness of the basis set near the nucleus (electric field gradient, NMR chemical shifts, etc.).

In view of these problems we developed recently [16] an approximate quasi-relativistic method which is variationally stable, can be easily implemented in any non-relativistic quantum-chemical program, leads to reliable relativistic corrections, and which requires low computational cost. This method, for which we coined the name LO-NESC-EP (low-order normalized elimination of small component using an effective potential) enables one to perform all-electron relativistic calculations on large molecular systems and to study beside properties that depend predominantly on the valence electrons also properties that depend on the core electrons (NMR chemical shifts, etc.). The development of LO-NESC-EP (or NECS-EP for brevity) has to be seen as a first step within a long term effort to obtain QM-MM methods suitable to predict the magnetic properties of large molecular systems of biochemical interest (enzymes, etc.) containing transition metal atoms or other heavy atoms. The development of a NESC-EP-DFT method as reported in this work represents the second step while further steps will focus on spin-orbit coupling corrections, the development of analytical gradients for routine optimization of molecular geometries, etc.

The low-order NESC approach [13,17] was chosen as a starting point because its one-electron equations can be easily formulated in the familiar form of the Schrödinger one-electron equation with relativistic correction terms for the potential energy and the metric [17]. Also, the calculation of the matrix elements of the Hamiltonian does not involve any unusual molecular integrals. Thus, the

low-order NESC approximation [17] is a suitable candidate for a merger with non-relativistic methods. The only problem of this quasi-relativistic method is its variational instability, because of which the low-order NESC approximation was previously abandoned [17].

As it has been shown in our recent publication [16], the situation can be changed by the use of an effective potential which, contrary to the nuclear–electron attraction potential commonly used in the relativistic correction to the potential energy, is regular near the atomic nucleus. The resulting NESC-EP approach is variationally stable and predicts atomic properties in a good agreement with relativistic four-component Dirac–Fock–Coulomb calculations. In the present communication, the NESC-EP method is extended to DFT in the form of relativistic Kohn–Sham method [5,6]. The basic formalism and details of the implementation are outlined in Sections 2 and 3. Also, results of first applications of NESC-EP-DFT are reported and compared with the available literature data (Section 4).

2. Theory

Relativistic Kohn–Sham (RKS) DFT [5,6] represents a general approach to the calculation of the ground-state properties of atomic and molecular systems which includes all relevant relativistic and quantum electrodynamical effects. Most often the RKS method is used in the so-called longitudinal no-sea approximation [18] which amounts to a neglect of both radiative and magnetic quantum electrodynamical corrections. This approximation is equivalent to the Dirac–Fock–Coulomb method [19] in wavefunction theory. The longitudinal no-sea RKS equations read

$$(v^{\text{RKS}} - \epsilon_k)\psi_k^{\text{L}} + c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_k^{\text{S}} = 0, \quad (1a)$$

$$c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi_k^{\text{L}} + (v^{\text{RKS}} - \epsilon_k - 2mc^2)\psi_k^{\text{S}} = 0, \quad (1b)$$

where ψ_k^{L} is the large and ψ_k^{S} is the small component of the four-component one-electron orbital $\psi_k = \begin{pmatrix} \psi_k^{\text{L}} \\ \psi_k^{\text{S}} \end{pmatrix}$, $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ the vector of the Pauli

matrices [20], $\mathbf{p} = -i\hbar\nabla$ the momentum operator, c the velocity of light, m the electron mass, and v^{RKS} the Kohn–Sham potential given by Eq. (2)

$$v^{\text{RKS}}(\mathbf{r}_1) = v_{\text{ext}}(\mathbf{r}_1) + v_H(\mathbf{r}_1) + v_{xc}([n], \mathbf{r}_1). \quad (2)$$

In Eq. (2) v_{ext} gives the external potential, which includes the nuclear–electron attraction and contributions from other external electric fields (if present); v_H is the potential of the classical Coulomb repulsion of electrons (3)

$$v_H(\mathbf{r}_1) = \int \frac{n(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 \quad (3)$$

and v_{xc} the exchange–correlation potential (4),

$$v_{xc}([n], \mathbf{r}_1) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r}_1)} \quad (4)$$

with n being the ground-state density and $E_{xc}[n]$ the exchange–correlation functional.

The NESC approach [13] is based on a replacement of the small component ψ_k^S in the Dirac equation [21] by the pseudolarge component ϕ_k^L

$$\psi_k^S = \frac{(\boldsymbol{\sigma} \cdot \mathbf{p})}{2mc} \phi_k^L. \quad (5)$$

Subsequently, the pseudolarge component ϕ_k^L is eliminated from the modified Dirac equations with the help of relation (6)

$$\phi_k^L = \hat{U} \psi_k^L, \quad (6)$$

which connects the large and the pseudolarge components by virtue of an energy-dependent non-unitary operator \hat{U} [13].

Applying Eq. (5) within the RKS scheme results in a modified RKS equation (7a) and (7b)

$$\hat{t} \phi_k^L + v^{\text{RKS}} \psi_k^L = \epsilon_k \psi_k^L, \quad (7a)$$

$$\hat{t} \psi_k^L + \frac{1}{4m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p})(v^{\text{RKS}} - \epsilon_k)(\boldsymbol{\sigma} \cdot \mathbf{p}) \phi_k^L = \hat{t} \phi_k^L, \quad (7b)$$

where \hat{t} is the kinetic energy operator (8)

$$\hat{t} = \frac{\mathbf{p}^2}{2m} = \frac{(\boldsymbol{\sigma} \cdot \mathbf{p})(\boldsymbol{\sigma} \cdot \mathbf{p})}{2m}. \quad (8)$$

Upon elimination of the pseudolarge component with the help of Eq. (6), Eq. (9) for the large component only emerges

$$\begin{aligned} & \left(\hat{t} - (\hat{I} - \hat{U}^\dagger) \hat{t} (\hat{I} - \hat{U}) + v^{\text{RKS}} \right. \\ & \left. + \frac{1}{4m^2 c^2} \hat{U}^\dagger (\boldsymbol{\sigma} \cdot \mathbf{p}) v^{\text{RKS}} (\boldsymbol{\sigma} \cdot \mathbf{p}) \hat{U} \right) \psi_k^L \\ & = \epsilon_k \left(1 + \frac{\hat{U}^\dagger \hat{t} \hat{U}}{2mc^2} \right) \psi_k^L. \end{aligned} \quad (9)$$

The non-unitary energy-dependent operator \hat{U} of Eqs. (6) and (9) possesses property (10) [13]

$$\hat{U} = \hat{I} + O(1/c^2), \quad (10)$$

where \hat{I} is the identity operator. This property enables one to define [17] a low-order approximation (correct to first-order in $1/c^2$) to Eq. (9). Thus, setting $\hat{U} = \hat{I}$ one gets Eq. (11) from Eq. (9); Eq. (11) is correct to order of $1/c^2$ and does no longer contain energy-dependent operators

$$\begin{aligned} & \left(\hat{t} + v^{\text{RKS}} + \frac{1}{4m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) v^{\text{RKS}} (\boldsymbol{\sigma} \cdot \mathbf{p}) \right) \psi_k \\ & = \epsilon_k \left(1 + \frac{\hat{t}}{2mc^2} \right) \psi_k. \end{aligned} \quad (11)$$

For the reason of brevity the superscript L labeling the large component has been dropped in Eq. (11).

Eq. (11) is analogous to the low-order NESC approximate equation [17] in the Dirac–Fock–Coulomb method and possesses the same variational properties, i.e., it is variationally unstable [17] when the usual nuclear–electron attraction potential $-Z/r$ is used in v_{ext} . Then, the relativistic correction to the nuclear–electron potential energy diverges as $-Z/r^3$ near the nucleus and prevails over the kinetic energy [17]. In the exact Eq. (9), the imbalance between kinetic and potential energies is prevented by the non-linear operator \hat{U} , which cuts off an excess in the energy of nuclear–electron attraction close to the nucleus. In our previous work [16], it was conjectured that this effect can be simulated in an approximate equation by the use of an (energy-independent) cut-off factor in the relativistic correction to the nuclear–electron attraction energy.

For this purpose it was proposed [16] to use potential (12)

$$v'_{Ne}(\mathbf{r}_1) = \sum_n^{\text{all } N} -\frac{Z_n}{r_{1n}} \text{erf}(r_{1n}/r_0(Z_n)) \quad (12)$$

instead of $v_{Ne}(\mathbf{r}_1) = \sum_n -Z_n/r_{1n}$ in the third term on the LHS of Eq. (11). In Eq. (12), $r_0(Z_n)$ is a cut-off radius specific for the n th nucleus and $r_{1n} = |\mathbf{r}_1 - \mathbf{r}_n|$ is the distance between the n th nucleus and the electron position given by radius-vector \mathbf{r}_1 . The error function in Eq. (12) cuts off the nuclear attraction potential at distances shorter than the cut-off radius $r_0(Z_n)$. The cut-off radius is of the order of the classical radius of the nucleus $Z/(mc^2)$. The dependence of the $r_0(Z_n)$ on the nuclear charge is given by Eq. (13) [16]

$$r_0(Z) = (a_0 + a_1 Z^{-1} + a_2 Z^{-2}) \frac{Z}{mc^2} \quad (13)$$

with the coefficients $a_0 = -0.263188$, $a_1 = 106.016974$, $a_2 = 138.985999$ being based on a fit of the $1s_{1/2}$ eigenvalues of the Dirac equation [21] for H-like atomic ions.

With potential (12), Eq. (11) modifies to Eq. (14)

$$\begin{aligned} & \left(\hat{t} + v_{Ne} + v_H + v_{xc} + \frac{1}{4m^2c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) v'_{Ne}(\boldsymbol{\sigma} \cdot \mathbf{p}) \right. \\ & \left. + \frac{1}{4m^2c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) (v_H + v_{xc}) (\boldsymbol{\sigma} \cdot \mathbf{p}) \right) \psi_k \\ & = \epsilon_k \left(1 + \frac{\hat{t}}{2mc^2} \right) \psi_k, \end{aligned} \quad (14)$$

where contributions to v_{ext} other than the nuclear–electron attraction are dropped for clarity. Eq. (14) differs from the corresponding equation of the Dirac–Fock–Coulomb formalism [16] only by using of the local multiplicative potentials v_H and v_{xc} instead of the non-local Hartree–Fock–Coulomb electron interaction potential. As these potentials are non-singular, their use in Eq. (14) does not threaten its variational stability and all conclusions drawn in our previous work [16] for an approximate quasi-relativistic equation within the Dirac–Fock–Coulomb formalism are equally valid for Eq. (14).

For the purpose of minimizing computational efforts when calculating the matrix elements of v_H and v_{xc} the one-electron part \mathbf{H}_1 of the quasi-rel-

ativistic Hamiltonian in Eq. (14) is renormalized on the non-relativistic metric [16] as given in matrix form by Eqs. (15a)–(15c)

$$\mathbf{H}'_1 = (\mathbf{S}^{1/2})^\dagger (\mathbf{X}^{-1/2})^\dagger \mathbf{H}_1 (\mathbf{X}^{-1/2}) (\mathbf{S}^{1/2}), \quad (15a)$$

$$X_{\mu\nu} = \left\langle \chi_\mu \left| 1 + \frac{\hat{t}}{2mc^2} \right| \chi_\nu \right\rangle, \quad (15b)$$

$$(H_1)_{\mu\nu} = \left\langle \chi_\mu \left| \hat{t} + v_{Ne} + \frac{1}{4m^2c^2} (\boldsymbol{\sigma} \cdot \mathbf{p}) v'_{Ne}(\boldsymbol{\sigma} \cdot \mathbf{p}) \right| \chi_\nu \right\rangle, \quad (15c)$$

where χ_ν are the basis functions used to expand the one-electron Kohn–Sham orbitals and \mathbf{S} is the matrix of the overlap integrals. Then, the one-electron quasi-relativistic Hamiltonian \mathbf{H}'_1 obtained in this way is used within the standard non-relativistic KS approach. As established for the Dirac–Fock–Coulomb formalism [16], such an approximation results in acceptably small upward shifts in the total energy, which even in the case of a He-like atomic ion with $Z = 100$ constitutes less than 0.1% of the total energy. Thus, it is Eqs. (15a)–(15c) together with Eqs. (12) and (13) that we propose to use within the standard non-relativistic KS approach to incorporate approximately the major relativistic effects.

3. Implementation and calculational details

With the help of the Dirac relation (16)

$$(\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i\boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}), \quad (16)$$

which is valid for any couple of vectors \mathbf{a} and \mathbf{b} not containing σ , Eq. (15c) can be split into a spin-free and a spin-dependent part as given in Eq. (17)

$$\begin{aligned} (H_1)_{\mu\nu} & = \left\langle \chi_\mu \left| \hat{t} + v_{Ne} + \frac{1}{4m^2c^2} \mathbf{p} \cdot v'_{Ne} \mathbf{p} \right| \chi_\nu \right\rangle \\ & + \left\langle \chi_\mu \left| \frac{i}{4m^2c^2} \boldsymbol{\sigma} \cdot (\mathbf{p} v'_{Ne}) \times \mathbf{p} \right| \chi_\nu \right\rangle. \end{aligned} \quad (17)$$

In the present work, we concentrate on the spin-free part of \mathbf{H}_1 and neglect the spin–orbit contribution in the last term on the r.h.s. of Eq. (17).

This scalar relativistic (one-component) approximation is sufficient for studies on closed shell molecular systems [22].

In the spin-free quasi-relativistic Hamiltonian \mathbf{H}_1 , the only part which is not covered by the existing non-relativistic quantum-chemical codes is the relativistic correction to the nuclear–electron attraction energy. Owing to the hermiticity of the momentum operator \mathbf{p} , the corresponding matrix elements can be transformed as in Eq. (18)

$$\begin{aligned} \frac{1}{4m^2c^2} \langle \chi_\mu | \mathbf{p} \cdot v'_{Ne} \mathbf{p} | \chi_\nu \rangle &= \frac{1}{4m^2c^2} \langle \chi_\mu | v'_{Ne} | \mathbf{p} \chi_\nu \rangle \\ &= \frac{\hbar^2}{4m^2c^2} \langle \nabla \chi_\mu | v'_{Ne} | \nabla \chi_\nu \rangle. \end{aligned} \quad (18)$$

The gradient of the Cartesian Gaussian type function (19)

$$\chi_\mu(l, m, n, \alpha) = N x^l y^m z^n e^{-\alpha r^2} \quad (19)$$

is expressed as a linear combination of Gaussian type functions with higher and lower angular momentum,

$$\begin{aligned} \nabla \chi_\mu(l, m, n, \alpha) &= N [\mathbf{i}(l\chi_\mu(l-1, m, n, \alpha) \\ &\quad - 2\alpha\chi_\mu(l+1, m, n, \alpha)) \\ &\quad + \mathbf{j}(m\chi_\mu(l, m-1, n, \alpha) \\ &\quad - 2\alpha\chi_\mu(l, m+1, n, \alpha)) \\ &\quad + \mathbf{k}(n\chi_\mu(l, m, n-1, \alpha) \\ &\quad - 2\alpha\chi_\mu(l, m, n+1, \alpha))], \end{aligned} \quad (20)$$

where \mathbf{i} , \mathbf{j} and \mathbf{k} are unit vectors along the x , y and z directions, respectively. Because the effective potential v'_{Ne} in Eqs. (12), (14), (15c), (17), (18) is a potential of a Gaussian charge distribution ρ_G (21)

$$\rho_G(\mathbf{r}_{1n}) = \sum_n^{\text{all } N} Z_n r_0(Z_n)^{-3} \pi^{-3/2} e^{-r_{1n}^2/r_0(Z_n)^2}, \quad (21)$$

the matrix elements (18) can be evaluated as a linear combination of the electron-repulsion integrals of type $(\chi_\mu \chi_\nu | ss)$. Thus, the evaluation of the matrix elements of the quasi-relativistic Hamiltonian \mathbf{H}_1 of Eq. (15c), can readily be done by slightly extending a non-relativistic quantum-chemical program.

However, a more economic way of calculating the matrix elements of \mathbf{H}_1 is based on the use of

modified nuclear-attraction integrals rather than the use of electron-repulsion integrals. The nuclear-attraction integrals $\langle \chi_\mu | v_{Ne} | \chi_\nu \rangle$ are routinely calculated [23] in terms of the auxiliary functions $F_\lambda([\alpha_\mu + \alpha_\nu] r_{pc}^2)$, where $F_\lambda(t)$ is given in Eq. (22)

$$F_\lambda(t) = \int_0^1 u^{2\lambda} e^{-tu^2} du. \quad (22)$$

With the help of the Fourier transform of the effective potential v'_{Ne} , it can be shown that the matrix elements $\langle \chi_\mu | v'_{Ne} | \chi_\nu \rangle$ can be calculated with the same formulae as the elements of v_{Ne} , but with the auxiliary functions F_λ replaced by $F_\lambda(\gamma r_{pc}^2 / (1 + \gamma r_0(Z_n)^2)) / (1 + \gamma r_0(Z_n)^2)^{\lambda+1/2}$, where $\gamma = \alpha_\mu + \alpha_\nu$. Thus, the incorporation of the proposed quasi-relativistic method into the existing non-relativistic quantum-chemical codes does not require calculation of unusual molecular integrals nor does it invoke any additional numeric integration and can be achieved at low cost.

The NESC-EP method was implemented into the COLOGNE 2001 suite of quantum-chemical programs [24]. Benchmark calculations were carried out for diatomic molecules AgH, Ag₂, CdH, CdH⁺, AuH, Au₂, HgH, and HgH⁺ where these molecules were chosen because spin–orbit coupling not considered in this work plays only a minor role in these cases [22]. All calculations employed uncontracted and contracted basis sets derived from the heavy element basis sets of Gropen [25] using recipes suggested by Nakajima and Hirao [12] and Hess and co-workers [26]. The uncontracted basis sets for Ag and Cd were augmented by one diffuse s-, three diffuse p-, and two diffuse d-type functions in an even-tempered sequence while for Au and Hg one s-, three p- and f-, and two d-type diffuse functions were added to the uncontracted basis sets of Gropen. The resulting (18s15p10d) (Ag, Cd) and (20s17p12d8f) basis sets (Au, Hg) were combined with Dunning's aug-cc-pVTZ basis set for hydrogen [27] (denoted in the following as U (uncontracted) basis set).

Smaller contracted basis sets for the heavy atoms were obtained from the generally contracted basis sets of Gropen as described in [12]. First, the innermost s-type function for Ag and Cd and the three innermost s-type functions for Au and Hg are uncontracted. Then, the outer-

most four *s*-, two *p*- and *d*-, and one *f*-type functions are uncontracted for all heavy atoms. The $(n+1)s$ function (n : principal quantum number of the valence *d*-orbital) is dropped for all atoms along with the *nd* orbital for Au and Hg. Finally, one *s*-, three *p*-, and one *d*-type diffuse functions for Ag and Cd, and one *s*-, three *p*- and *d*-, and two *f*-type diffuse functions for Au and Hg are added in an even-tempered sequence. The resulting contracted [10s8p5d] (Ag, Cd) and [13s9p6d4f] basis sets (Au, Hg) are combined with Dunning's aug-cc-pVDZ basis set for hydrogen [27] (denoted in the following as C (contracted) basis set).

In the Kohn–Sham calculations the B3LYP hybrid functional [28] was used. Equilibrium internuclear distances and harmonic vibrational frequencies were obtained numerically in the quasi-relativistic and analytically in the non-relativistic calculations. Dissociation energies were calculated as the energy difference between the isolated atoms and the molecule. For open-shell systems the spin-unrestricted DFT approach was used.

4. Results and discussion

The calculated spectroscopic constants of the AgH, Ag₂, CdH, CdH⁺, AuH, Au₂, HgH, and HgH⁺ molecules are presented in Table 1. On the average, the results of the quasi-relativistic B3LYP calculations are in a reasonably good agreement with experimental values [29]. The mean absolute deviations in the calculated bond lengths (U: 0.015; C: 0.010 Å), vibrational frequencies (U: 36; C: 53 cm⁻¹) and dissociation energies (U: 0.09; C: 0.13 eV, Table 1) are within the ballpark typical for the non-relativistic B3LYP calculations on compounds of light elements [30]. It has to be noted that the calculated vibrational frequencies are obtained in the harmonic approximation whereas for a better comparison with experimental frequencies also anharmonicity effects should be included into calculated frequencies. Normally, harmonic vibrational frequencies are larger than the observed ones.

The non-relativistic B3LYP results are in a poor agreement with the experimental data (mean deviations for U: 0.135 Å, 216 cm⁻¹, 0.64 eV; for C: 0.135 Å, 213 cm⁻¹, 0.56 eV; Table 1). For the diatomic molecules including Ag and Cd, the non-relativistic B3LYP dissociation energies (deviations of ≤ 0.3 eV, Table 1) are acceptable. However, even in these cases bond lengths and vibrational frequencies are out of range of accuracy typical of DFT/B3LYP calculations for lighter elements [30]. For the diatomics involving Au and Hg, deviations in the bond lengths are up to 0.3 Å, in the stretching frequencies up to 700 cm⁻¹, and in the dissociation energies up to 1.5 eV (Table 1) underlining the necessity of relativistic corrections. Thus, the NESC-EP-DFT method furnishes a substantial improvement over the non-relativistic DFT calculations.

A comparison with the performance of other quasi-relativistic methods implies that calculations are done with the same basis sets and density functional. Thus, a comparison with ZORA method is quite difficult, because the available results are obtained with the BP86 functional using a basis of Slater-type functions [10]. In such a case, it is difficult to discriminate effects which stem from differences in density functionals or in the basis sets used, from those caused by differences in the quasi-relativistic computational schemes. The only data available from the literature which can be directly compared with those reported in Table 1 are the results of RESC-B3LYP calculations of molecules AgH and AuH [12]. RESC-B3LYP calculations are also reported [30] for Ag₂ and Au₂, but these calculations employ a somewhat different (albeit of comparable size) contracted basis set. The RESC-B3LYP calculations yield for AgH [12]: $r_e = 1.631$ Å, $\omega_e = 1761$ cm⁻¹, $D_e = 2.44$ eV; for AuH [12]: $r_e = 1.527$ Å, $\omega_e = 2328$ cm⁻¹, $D_e = 3.40$ eV; for Ag₂ [30]: $r_e = 2.596$ Å, $\omega_e = 176$ cm⁻¹, $D_e = 1.52$ eV; and for Au₂ [30]: $r_e = 2.507$ Å, $\omega_e = 185$ cm⁻¹, $D_e = 2.57$ eV. These data have to be compared with the NESC-EP-B3LYP contracted basis set results listed in Table 1.

The results of quasi-relativistic B3LYP calculations based on the Douglas–Kroll–Hess (DKH) approximation [8,9] are available for Au₂ [32]. These calculations used an uncontracted (21s17

Table 1
Spectroscopic constants of some diatomic molecules^a

Molecule	Method	r_e (Å)	ω_e (cm ⁻¹)	D_e (eV)
AgH	NESC-EP-B3LYP/U	1.620 (1.694)	1775 (1584)	2.37 (2.15)
	NESC-EP-B3LYP/C	1.627 (1.699)	1808 (1606)	2.36 (2.15)
	exp.	1.618	1760	2.39
Ag ₂	NESC-EP-B3LYP/U	2.581 (2.670)	183 (153)	1.56 (1.38)
	NESC-EP-B3LYP/C	2.569 (2.660)	190 (157)	1.63 (1.41)
	exp.	2.531	192	1.67
CdH	NESC-EP-B3LYP/U	1.791 (1.823)	1380 (1415)	0.79 (0.94)
	NESC-EP-B3LYP/C	1.787 (1.818)	1396 (1429)	0.80 (0.96)
	exp.	1.781	1337	0.76
CdH ⁺	NESC-EP-B3LYP/U	1.668 (1.721)	1807 (1685)	2.15 (1.98)
	NESC-EP-B3LYP/C	1.668 (1.720)	1841 (1707)	2.16 (1.97)
	exp.	1.667	1772	2.20
AuH	NESC-EP-B3LYP/U	1.502 (1.734)	2458 (1642)	3.54 (2.24)
	NESC-EP-B3LYP/C	1.524 (1.723)	2391 (1631)	3.32 (2.21)
	exp.	1.524	2305	3.36
Au ₂	NESC-EP-B3LYP/U	2.464 (2.761)	195 (122)	2.46 (0.81)
	NESC-EP-B3LYP/C	2.469 (2.775)	197 (124)	2.78 (1.47)
	exp.	2.472	191	2.29
HgH	NESC-EP-B3LYP/U	1.764 (1.863)	1221 (1468)	0.43 (0.93)
	NESC-EP-B3LYP/C	1.761 (1.870)	1192 (1418)	0.60 (0.89)
	exp.	1.766	1203	0.45
HgH ⁺	NESC-EP-B3LYP/U	1.569 (1.769)	2035 (1679)	3.14 (2.00)
	NESC-EP-B3LYP/C	1.591 (1.770)	1888 (1623)	2.93 (1.98)
	exp.	1.594	2028	3.12
mae/std ^b	NESC-EP-B3LYP/U	0.015/0.023	36/62	0.09/0.11
		(0.135/0.168)	(216/312)	(0.64/0.86)
	NESC-EP-B3LYP/C	0.010/0.015	53/73	0.13/0.21
		(0.135/0.169)	(213/318)	(0.56/0.73)

^a Calculated with an uncontracted (U) or contracted (C) basis set. Non-relativistic B3LYP results in parentheses. Experimental values from [29].

^b Mean absolute deviation (mae) and standard deviation (std) of calculated properties from experimental values.

p11d7f) basis set [26] which differs from the uncontracted (20s17p12d8f) basis used in the present work by the absence of very tight s-type basis functions; otherwise, the two basis sets are large enough to make a direct comparison of the results of DKH-B3LYP and NESC-EP-B3LYP meaningful. The DKH-B3LYP method yields for Au₂ [31]: $r_e = 2.541$ Å, $\omega_e = 169$ cm⁻¹, $D_e = 2.03$ eV.

The aforementioned results suggest that the DKH-DFT method [8,9] underestimates the relativistic corrections to the spectroscopic constants, whereas the RESC-DFT and NESC-EP-DFT methods lead to descriptions of approximately the same quality. However, the RESC approach is variationally unstable in the sense that adding of

the tight basis functions results in a variational collapse [14]. Thus, it is impossible to obtain (with respect to the basis set size) converged results using RESC. This is important when calculating properties which depend strongly on the basis set completeness (see above). At the same time the NESC-EP method is variationally stable and allows for an augmentation of the basis set with tight functions.

5. Conclusions

The NESC-EP approach proposed previously was combined with DFT for solving the Dirac–Kohn–Sham problem within the longitudinal

no-sea approximation. Test calculations on AgH, Ag₂, CdH, CdH⁺, AuH, Au₂, HgH, and HgH⁺ molecules reveal that NESC-EP-DFT is a computationally efficient and reliable new quasi-relativistic method. Calculated equilibrium bond lengths, vibrational frequencies, and dissociation energies obtained with NESC-EP-B3LYP are of comparable accuracy for molecules containing heavy elements as they are for molecules containing first and second row elements when using standard Kohn–Sham DFT with the B3LYP hybrid functional. Thus, the new method provides a balanced treatment of relativistic effects for molecular properties.

Apart from its accuracy, an important feature of the new method is its simplicity both in the sense of implementation and in the sense of computational cost. The matrix elements of the NESC-EP-DFT Hamiltonian do not involve any unusual molecular integrals often appearing in relativistic calculations; they can be evaluated analytically using the existing non-relativistic quantum-chemical software. Since all modifications concern the one-electron Hamiltonian only, the results of relativistic calculation can be obtained at essentially the cost of a non-relativistic calculation.

As the NESC-EP-DFT method treats all electrons explicitly, it can be used for the calculation of magnetic shielding tensors of heavy elements in large molecular systems. This goal will be pursued in a subsequent work along with an implementation of analytic energy gradients for the new method and the calculation of molecular excitation properties.

Acknowledgements

This work was supported by the Swedish Natural Science Research Council (NFR). Calculations were done on the supercomputers of the Nationellt Superdatorcentrum (NSC), Linköping, Sweden.

References

- [1] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [2] R.M. Dreizler, E.K.U. Gross (Eds.), *Density Functional Theory*, NATO ASI Series B: Physics, vol. 337, Plenum Press, New York, 1995.
- [3] P. Pyykkö, *Chem. Rev.* 97 (1997) 597.
- [4] J. Almlöf, O. Gropen, in: K.B. Lipkowitz, D.B. Boyd (Eds.), *Reviews in Computational Chemistry*, vol. 8, VCH, New York, 1996, p. 203.
- [5] A.K. Rajagopal, *J. Phys. C* 11 (1978) L943.
- [6] A.H. MacDonald, S.H. Vosko, *J. Phys. C* 12 (1979) 2977.
- [7] L.L. Foldy, S.A. Wouthuysen, *Phys. Rev.* 78 (1950) 29.
- [8] M. Douglas, N.M. Kroll, *Ann. Phys. (NY)* 82 (1974) 89.
- [9] B.A. Hess, *Phys. Rev. A* 33 (1986) 3742.
- [10] E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* 101 (1994) 9783.
- [11] C. van Wüllen, *J. Chem. Phys.* 109 (1998) 392.
- [12] T. Nakajima, K. Hirao, *Chem. Phys. Lett.* 302 (1999) 383.
- [13] K.G. Dyall, *J. Chem. Phys.* 106 (1997) 9618.
- [14] M. Barysz, *J. Chem. Phys.* 113 (2000) 4003.
- [15] J.H. van Lenthe, S. Faas, J.G. Snijders, *Chem. Phys. Lett.* 328 (2000) 107.
- [16] M. Filatov, D. Cremer, *J. Chem. Phys.*, submitted.
- [17] K.G. Dyall, *J. Chem. Phys.* 109 (1998) 4201.
- [18] E. Engel, S. Keller, A. Facco Bonetti, H. Müller, R.M. Dreizler, *Phys. Rev. A* 52 (1995) 2750.
- [19] B. Swirles, *Proc. Roy. Soc. (London) A*. 152 (1935) 625.
- [20] W. Pauli, *Z. Physik* 43 (1927) 601.
- [21] P.A.M. Dirac, *Proc. Roy. Soc. (London) A* 117 (1928) 610.
- [22] E. van Lenthe, J.G. Snijders, E.J. Baerends, *J. Chem. Phys.* 105 (1996) 6505.
- [23] H. Taketa, S. Huzinaga, K. Oohata, *J. Phys. Soc. Jpn.* 21 (1966) 2313.
- [24] E. Kraka, J. Gräfenstein, J. Gauss, M. Filatov, V. Polo, F. Reichel, L. Olsson, Z. Konkoli, Z. He, D. Cremer, *COLOGNE 2001*, Göteborg University, Göteborg, 2001.
- [25] O. Gropen, *J. Comput. Chem.* 8 (1987) 982.
- [26] A. Pizlo, G. Jansen, B.A. Hess, W. von Niessen, *J. Chem. Phys.* 98 (1993) 3945.
- [27] T.H. Dunning Jr., *J. Chem. Phys.* 90 (1989) 1007.
- [28] P.J. Stephens, F.J. Devlin, C.F. Chabrowski, M.J. Frish, *J. Phys. Chem.* 98 (1994) 11623.
- [29] K.P. Huber, G. Herzberg, *Molecular Spectra and Molecular Structure*, vol. IV, Constants of Diatomic Molecules, Van Nostrand, Princeton, NY, 1979.
- [30] L.A. Curtiss, K. Raghavachari, P.C. Redfern, J.A. Pople, *J. Chem. Phys.* 112 (2000) 7374.
- [31] S. Yanagisawa, T. Tsuneda, K. Hirao, *J. Comput. Chem.* 22 (2001) 1995.
- [32] Y.-K. Han, K. Hirao, *Chem. Phys. Lett.* 324 (2000) 453.