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A singularity excluded approximate expansion scheme in relativistic density functional theory

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Abstract. A singularity excluded approximate expansion (SEAX) scheme, which can be considered as one between Breit-Pauli expansion and RA expansion schemes, is proposed to expand the total energy of 4-component relativistic density functional theory. The one-electron equation can be derived variationally from the approximate total energy expression. The Hamiltonian of the one-electron equation is bounded from below and can be dealt with variationally, and the gauge dependency error in the ZORA method is essentially eliminated. It is easier to solve the SEAX equation than the IORA equation. The results related to the valence orbitals by solving the scalar SEAX equation agree very well with those by the scalar ZORA ESA method, and the results related to the inner-shell electrons of heavy elements by the two component SEAX calculations agree quite well with those by the 4-component relativistic density functional calculations.

Key words: Quantum chemical calculations – Relativistic effects – Dirac operator – Approximate expansion – Density functional theory – Kohn-Sham equation

Introduction

It has been recognized that relativistic effects influence significantly the properties of heavy elements [1]; thus, the relativistic effects have to be considered in the theoretical study of compounds containing heavy elements, for which the Dirac equation has to be solved instead of solving the Schroedinger equation. Although the first principle methods and programs for solving the Dirac equation have been developed, only quite small molecules have been studied with these methods because the related calculations are very time-consuming [2–6]. To surmount this obstacle people have sought approximate approaches that incorporate the major relativistic effects, but which demand much less computational effort. Several such approaches have been proposed [7–18]. The approaches based on regular approximation (RA) such as ZORA and IORA, etc. [13, 14, 19] are attractive for the fact that the effective Hamiltonian of the one-electron equations is simple, bounded from below and variationally stable [20, 21]. Their computational effort is only slightly larger than the correspondent non-relativistic calculations, while the calculated results are satisfactory [22]. There are three problems in RA schemes arising from the fact that the potential term is involved in the denominator of the kinetic energy operator. The first is that the ZORA total energy is not stationary with respect to orbital variations. The second is that the ZORA equation is not gauge invariant which leads to errors in energy difference calculations. The third is that the kinetic energy matrix needs evaluating in each cycle of iteration leading to increase of computational efforts. To circumvent the third problem Philipsen PHT et al. [23] proposed to use the sum of atomic potentials to approximate the potential term in the kinetic energy operator (SAPA). When more accurate potential in the kinetic energy operator is required they adopted better-fixed potential, which is close to the molecular potential but does not depend on the molecular orbitals. It is found that in combined use of the scaled (SR) ZORA method and the electrostatic shift approximation (ESA), the error in the energy difference calculations due to the gauge dependency in ZORA method can be reduced to be tolerable [14]. Van Wüllen [24] pointed out that using the superposition of atomic potentials as the approximate potential in the kinetic energy operator is unsuitable because the exchange-correlation potential is not linear in the electron density, and that there are some points unreasonable in the ZORA ESA method. He proposed the ZORA (MP) [24] method, in which the potential produced by the superposition of the spherical model atomic charge densities is used as the approximate potential in the kinetic energy operator, and claimed that all three problems above mentioned were satisfactorily solved. However, van Lenthe et al. [25] pointed out

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that a small gauge dependence problem still exists in the ZORA (MP) method and suggested that a possible approach to solve the gauge dependence problem would be to construct a model potential such that the electrostatic shift is zero for an atom due to other atoms in the regions. In the previous paper we proposed the ZORA (SLF) scheme [26] in which a space-limited potential function is used in the ZORA kinetic energy operator. It was found that the gauge dependence errors in the calculated bond lengths and binding energies by ZORA (SLF) method are reduced to comparable with those of ZORA ESA method. However, the calculated molecular properties in connection with the deeper inner electrons by the ZORA (SLF) method is not quite good, while it is needed sometimes to study the subjects related to the deeper inner shells of heavy elements. The IORA method can give quite accurate results even for the properties related to the inner shells of very heavy atoms. But there are some problems left unsolved, particularly, the one-electron equation is not variationally connected to the molecular total energy, which may result in some difficulty in the analytical gradient calculations, and the potential term in the kinetic energy operator leads to computational trouble. The IORA method has not yet been used in the calculations of molecules to the best of our knowledge. In the present paper, a singularity excluded approximate expansion (SEAX) scheme, which can be considered as one between the Breit-Pauli expansion and the RA expansion schemes, is proposed to expand the total energy of the 4-component relativistic density functional theory. An approximate expression for the total energy can be obtained by use of the SEAX scheme, from which the one-electron equation can be variationally derived. Less computational efforts are needed for solving the SEAX one-electron equation than the IORA equation. In the calculations of a series of molecules with the SEAX method it is found that the gauge dependence error can be essentially eliminated and the calculated results are quite satisfactory even for the properties related to the deeper inner shell electrons. Firstly, the basic equation will be derived and its main properties will be discussed. Then, the calculated results for some atoms and molecules will be presented and compared with those by other approximate methods and the 4-component relativistic density functional (DF) method. Finally, we present some concluding remarks.

Basic equation

The total energy of molecules or atoms in density functional theory can be written as

$$E = \sum_i \langle \psi_i | \hat{T} | \psi_i \rangle + \sum_i \langle \psi_i | V_N | \psi_i \rangle + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 + E_{xc}[\rho] \tag{1}$$

where $\hat{T}$ is the kinetic operator, V_{N} is the nuclear potential, E_{XC} is the exchange-correlation energy, and $\rho(\vec{r}) = \sum_i \langle \psi_i | \vec{r} \rangle \langle \vec{r} | \psi_i \rangle$is the electronic density. In the relativistic density functional calculations, the relativistic correction to E_{XC} is usually neglected because it does not exhibit significant effects on valence electronic properties and the non-relativistic formulas for E_{XC} is used in practical calculations [13, 19]. In the 4-component relativistic density functional theory, $\hat{T} = \begin{pmatrix} 0 & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & -2c^2 \end{pmatrix}$ and ψ_{i} satisfies the Dirac-Kohn-Sham equation:

$$\left[\begin{pmatrix} 0 & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & -2c^2 \end{pmatrix} + V \right] \psi_i = \varepsilon_i \psi_i \tag{2}$$

where $V = V_N + V_{Coul} + V_{XC}$, $V_N = \sum_A V_N^A$ is the nuclear attractive potential, $V_{Coul} = \int \frac{\rho(\vec{r}_2)}{|\vec{r} - \vec{r}_2|} d^3r_2$ is the Coulomb potential, $V_{XC} = \frac{\delta E_{XC}}{\delta \rho}$ is the exchange-correlation potential, the Breit term is neglected as usual. $\{\psi_i\}$ are 4-component wavefunctions and each can be written as $\psi_i = \begin{pmatrix} \phi_i^L \\ \phi_i^S \end{pmatrix}$, ϕ_i^L and ϕ_i^S are the large and small components respectively and they are both 2-component wavefunctions. From Eq. (2) it can be obtained that

$$\phi_i^S = \frac{c}{2c^2 - V + \varepsilon_i} \vec{\sigma}\cdot\vec{p}\phi_i^L \tag{3}$$

By use of Eq. (3) and $\psi_i = \begin{pmatrix} \phi_i^L \\ \phi_i^S \end{pmatrix}$, Eq. (1) can be written as

$$\begin{aligned} E = \sum_i \{ & \langle \phi_i^L | V_N | \phi_i^L \rangle + \langle \phi_i^L | \vec{\sigma}\cdot\vec{p} \frac{c^2 V_N}{(2c^2 - V + \varepsilon_i)^2} \vec{\sigma}\cdot\vec{p} | \phi_i^L \rangle \\ & + \langle \phi_i^L | \vec{\sigma}\cdot\vec{p} \frac{2c^2}{2c^2 - V + \varepsilon_i} \vec{\sigma}\cdot\vec{p} | \phi_i^L \rangle \\ & - \langle \phi_i^L | \vec{\sigma}\cdot\vec{p} \frac{2c^4}{(2c^2 - V + \varepsilon_i)^2} \vec{\sigma}\cdot\vec{p} | \phi_i^L \rangle \} \\ & + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 + E_{XC}[\rho] \end{aligned} \tag{4}$$

where

$$\begin{aligned} \rho(\vec{r}) = \sum_i \Big\{ & \langle \phi_i^L | \vec{r} \rangle \langle \vec{r} | \phi_i^L \rangle \\ & + \left\langle \phi_i^L | \vec{\sigma}\cdot\vec{p} \frac{c^2}{(2c^2 - V + \varepsilon_i)^2} \middle| \vec{r} \right\rangle \langle \vec{r} | \vec{\sigma}\cdot\vec{p} | \phi_i^L \rangle \Big\} \end{aligned} \tag{5}$$

The orthonormal conditions for $\{\phi_i^L\}$ are

$$\begin{aligned} & \left\langle \phi_j^L | \phi_j^L \right\rangle \\ & + \left\langle \phi_j^L \middle| \vec{\sigma}\cdot\vec{p} \frac{c^2}{(2c^2 - V + \varepsilon_j)(2c^2 - V + \varepsilon_i)} \vec{\sigma}\cdot\vec{p} \middle| \phi_i^L \right\rangle = \delta_{ij} \end{aligned} \tag{6}$$

The term $\frac{1}{2c^2 - V + \varepsilon_i}$ in Eqs. (4), (5), and (6) can be expanded in the following way:

$$\begin{aligned} \frac{1}{2c^2 - V + \varepsilon_i} & = \frac{1}{2c^2 - V_0 - \Delta V + \varepsilon_i} \\ & = \frac{1}{(2c^2 - V_0)} \left(1 + \frac{\varepsilon_i - \Delta V}{2c^2 - V_0} \right)^{-1} \\ & = \sum_{k=0}^{\infty} \frac{(\Delta V - \varepsilon_i)^k}{(2c^2 - V_0)^{k+1}} \end{aligned} \tag{7}$$

where $\Delta V = V - V_0$. It should be noted that V_0 need not be a model or effective potential; it is just a function used to exclude the Coulomb singularities in the nuclear positions. If $V_0 = V$ is assumed, Eq. (7) becomes the expansion formula used in the regular approximation, which leads to gauge dependency difficulty in the ZORA method [13] and makes it difficult to derive the one-electron equation from the total energy expression. When $V_0 = 0$, Eq. (7) is equivalent to the expansion scheme used to obtain the Breit-Pauli Hamiltonian, in which there are singularities in the nuclear positions and the expansion is invalid in the regions very near the nuclei. Our choice is to construct the V_0 in Eq. (7) appropriately to exclude the singularities appearing in the Breit-Pauli expansion. The V_0 should be close to the nuclear potential in regions near the nuclei for removing the nuclear potential singularity as far as possible, and it should be very near zero in other regions for reducing the gauge dependent errors. Concretely, it is taken as a truncated nuclear potential:

$$V_0 = \sum_A V_0^A, \quad V_0^A = V_N^A\left\{1 + \exp\left[\alpha\left(r - r_0^A\right)\right]\right\}^{-1} \tag{8}$$

where V_N^A is the potential of nucleus A, r_0^A is a given small value proper to nucleus A, and α is a large enough positive number. Obviously the aforementioned requirements for V_0 are satisfied. Furthermore, the derivative of V_0 given by Eq. (8) with respect to coordinates is simple, which facilitate the evaluation of analytical energy gradients. It is found in calculation practices that the calculated results are insensitive to the parameters r_0^A and α to a certain extent. Expanding Eqs. (4), (5), and (6) by use of Eq. (7) and neglecting the $\mathrm{O}((2c^2 - V_0)^{-3})$ and higher degree terms, the total energy can be approximately written as

$$\begin{aligned} E^{(1)} = \sum_i \Bigg\{ & \langle \phi_i^L | V_N | \phi_i^L \rangle + \left\langle \phi_i^L \middle| \vec{\sigma} \cdot \vec{p} \frac{c^2 V_N}{(2c^2 - V_0)^2} \vec{\sigma} \cdot \vec{p} \middle| \phi_i^L \right\rangle \\ & + \left\langle \phi_i^L \middle| \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 - V_0)} \vec{\sigma} \cdot \vec{p} \middle| \phi_i^L \right\rangle \\ & - \left\langle \phi_i^L \middle| \vec{\sigma} \cdot \vec{p} \frac{c^2 V_0}{(2c^2 - V_0)^2} \vec{\sigma} \cdot \vec{p} \middle| \phi_i^L \right\rangle \Bigg\} \\ & + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2 + E_{xc}[\rho] \end{aligned} \tag{9}$$

and the electronic density is

$$\begin{aligned} \rho(\vec{r}) \approx \sum_i \Bigg\{ & \langle \phi_i^L | \vec{r} \rangle \langle \vec{r} | \phi_i^L \rangle \\ & + \langle \phi_i^L | \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 - V_0)^2} | \vec{r} \rangle \langle \vec{r} | \vec{\sigma} \cdot \vec{p} | \phi_i^L \rangle \Bigg\} \end{aligned} \tag{10}$$

The orthonormal conditions become

$$\left\langle \phi_j^L | \phi_i^L \right\rangle + \left\langle \phi_j^L \middle| \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 - V_0)^2} \vec{\sigma} \cdot \vec{p} \middle| \phi_i^L \right\rangle = \delta_{ij} \tag{11}$$

Making $E^{(1)}$ stationary respect to ϕ_i^L's variation with the constraint Eq. (11) the following one-electron equation can be obtained:

$$\begin{aligned} & \left[\vec{\sigma} \cdot \vec{p} \frac{c^2}{2c^2 - V_0} \vec{\sigma} \cdot \vec{p} - \vec{\sigma} \cdot \vec{p} \frac{c^2 V_0}{(2c^2 - V_0)^2} \vec{\sigma} \cdot \vec{p} \right. \\ & \quad \left. + \vec{\sigma} \cdot \vec{p} \frac{c^2\, V}{(2c^2 - V_0)^2} \vec{\sigma} \cdot \vec{p} + V \right] \phi_i^L \\ & \quad = \varepsilon_i \left[1 + \vec{\sigma} \cdot \vec{p} \frac{c^2}{(2c^2 - V_0)^2} \vec{\sigma} \cdot \vec{p} \right] \phi_i^L \end{aligned} \tag{12}$$

The electronic density used to calculate V is obtained from Eq. (10). Equation (12) is the basic equation of the SEAX method. It can be seen that Eq. (12) is just the IORA equation when $V_0 = V$, but in that case Eq. (12) cannot be derived variationally from the total energy expression because V is involved in the denominators and related to $\{\phi_i^L\}$. When V_0 is taken as zero and Eq. (12) is further transformed to eliminate the metric term in the r.h.s., one can obtain the Breit-Pauli Hamiltonian. In the present paper, V_0 is constructed as mentioned above and Eq. (12) is not transformed further. The calculations are carried out directly using Eq. (12). Since the kinetic energy matrix and the metric matrix need evaluating only once, the computational effort for solving Eq. (12) is less than that for solving the IORA equation. Furthermore, based on Eq. (9) the expression of the analytical energy gradient can be derived and implemented without difficulty. Obviously if the $\mathrm{O}((2c^2 - V_0)^{-2})$ term is also neglected, Eq. (12) becomes

$$\left(\vec{\sigma} \cdot \vec{p} \frac{c^2}{2c^2 - V_0} \vec{\sigma} \cdot \vec{p} + V \right) \phi_i^L = \varepsilon_i \phi_i^L \tag{13}$$

which is similar to the ZORA (SLF) equation. It is the non-relativistic Kohn-Sham equation if $V_0 = 0$. It becomes the ZORA (MP) equation when V_0 is taken as van Wüllen's model potential, but the gauge dependence error cannot be completely eliminated. When $V_0 = V$, Eq. (13) is the ZORA equation, but again in that case it cannot be derived variationally from the total energy expression.

Following Refs. [19–21], it can be shown that the Hamiltonian in Eq. (12) is bounded from below and is variationally stable. As pointed out by Kutzelnigg [27] the RA Hamiltonian are not bounded from below by the exact one-electron energy, rather by an energy below it, and the deviation is of $\mathrm{O}(c^{-4})$. The SEAX Hamiltonian would have a similar behavior. In fact, the 4-component relativistic methods with kinetic balance bases [28, 29] to avoid variational collapse bear the same problem. Since the deviation is quite small, the calculated one-electron energies from Eq. (12) can still be considered as a good approximation to the exact ones.

It is worthwhile to note that the SEAX approach can be considered as an approximate 4-component relativistic density functional method for the positive energy states with the constraint that the relation between the small and large components is fixed by an approximate formula which is independent of energy and wavefunctions and satisfies the kinetic balance condition. Thus, only the Dirac-Kohn-Sham equation for the large components (Eq. (12)) needs solving and it can be done so variationally. Therefore, the computational efforts of the SEAX method are reduced greatly relative to the method to solve the 4-component Dirac-Kohn-Sham equation. Furthermore, like the IORA method, the evaluation of molecular properties is simple in the SEAX scheme due to no need of picture changes [30, 31].

Obviously, variation of V_0 influences both $E^{(1)}$ and the eigenvalues (ε_i) in Eq. (12). But, it can be shown that when V_0 changes to $V_0 + \delta V_0$, the changes of electronic density, the Coulomb, and exchange-correlation potentials, $E^{(1)}$ and ε_is are all of $O(c^{-4})$; thus, these quantities are not sensitive to the variation of V_0, and the calculated result of the SEAX method is insensitive to the choice of the parameters to define V_0.

The SEAX method is also not gauge invariant as in the ZORA and IORA methods since V and V_0 should have the same gauge to make Eq. (7) of meaning while V_0 is in the denominator. However, the gauge dependency error in the calculation of energy differences with the SEAX method is negligible. For example, in the calculation of molecular binding energies, the V_0 values are different for the molecule and its constituent atoms; the gauge dependency error δE_b can be written as:

$$\delta E_b = \sum_A \sum_i \langle \phi_i^A | \vec{\sigma}\cdot\vec{p}\, \frac{2c^2 (V_N^A - V_0)\Delta V_0}{(2c^2 - V_0)^3}\, \vec{\sigma}\cdot\vec{p} | \phi_i^A \rangle \qquad (14)$$

where ϕ_i^A is the large component of orbital i of atom A, $\Delta V_0 = V_0^A - V_0 = \sum_{B \neq A} (-V_0^B)$ for atom A. It can be seen that δE_b is of $O(c^{-4})$. Furthermore, with the appropriate construction of V_0 in the present paper, $V_N^A - V_0 \approx 0$ in the region near nucleus A, while in other regions $\Delta V_0 \approx 0$ except for the small spaces around the nuclei other than nucleus A in the molecule. The contribution from these small spaces to the integral related to atom A is very small. Then δE_b must be a very small quantity and can be negligible. Thus, the gauge dependency trouble in the ZORA method is essentially eliminated in the SEAX method.

The scalar SEAX equation can be obtained by separating the terms containing spin operator from Eq. (12).

$$\left[\vec{p}\frac{c^2}{2c^2 - V_0}\vec{p} - \vec{p}\frac{c^2\, V_0}{(2c^2 - V_0)^2}\vec{p} + \vec{p}\frac{c^2\, V}{(2c^2 - V_0)^2}\vec{p} + V \right] \psi_i = \varepsilon_i \left[1 + \vec{p}\frac{c^2}{(2c^2 - V_0)^2}\vec{p} \right] \psi_i \qquad (15)$$

And the electronic density in this case can be written as

$$\rho(\vec{r}) = \sum_i \left\{ \langle \psi_i | \vec{r} \rangle \langle \vec{r} | \psi_i \rangle + \langle \psi_i | \vec{p}\frac{c^2}{(2c^2 - V_0)^2} | \vec{r} \rangle \langle \vec{r} | \vec{p} | \psi_i \rangle \right\} \qquad (16)$$

The simplified scheme for solving the ZORA equation [32] can also be used in the SEAX method, that is, Eq. (15) is solved first, then the spin-orbit interaction terms are involved in the Hamiltonian and the iteration is continued to convergence to obtain the solution of Eq. (12).

The computational efforts will increase considerably if the second term in the r.h.s of Eqs. (10) or (16) is taken into account in calculating the gradient correction of exchange-correlation energies because the second order differentials of basis sets are required. This term is of $O(c^{-2})$; its contribution to the electron density gradient is quite small and its contribution to the non-local correction of exchange-correlation energies must be quite small too. With this fact in mind the contribution of the second term in the r.h.s of Eqs. (10) or (16) to the non-local correction of exchange-correlation energies can be neglected in practical calculations.

Results and discussions

Calculated result for atoms

The orbital energies of U and Pu are calculated with Eq. (12). The V_0 is taken as a truncated nuclear potential as mentioned above.

$$V_0^A = \frac{V_N^A}{1 + \exp[\alpha(r - r_0)]} \qquad (17)$$

with $\alpha = 300$ and $r_0 = 0.1$ a.u. It has been shown that the calculated result is insensitive to the values of α and r_0. Equation (12) is solved by the basis set expansion method, the universal Gaussian basis set [33] is used, and the Xα exchange-correlation potential with $\alpha = 0.7$ is adopted. All the matrix elements are calculated with numerical integration methods and the Gauss-Chebeshev quadrature is used. The calculated orbital energies are listed in Tables 1 and 2. The calculated results of Pu by the ZORA and IORA methods with the same computational details and by numerically solving the 4-component Dirac-Slater equation as well as the relevant results of U in the references are also listed in the tables for comparison. It can be seen that ZORA, IORA, SEAX, and Dirac-Slater methods give very similar valence orbital energies. The orbital energies by the SEAX method are all lower than the correspondent eigenvalues of the Dirac-Slater equation within numerical calculation errors, showing that the SEAX Hamiltonian is bounded from below by an energy below the exact one, the deeper the orbitals, the larger the deviation. However, the deviation is small, except for the 1s orbital; the largest deviation is only about 0.1% and it becomes negligible from the 3s orbital outwards. ZORA and IORA methods show the similar behavior, and the ZORA method has the largest deviation. The agreement between the results by the IORA method and from the Dirac-Slater calculation is better, though there is no significant difference between the results from the IORA and SEAX methods except for the 1s orbital. The inner orbital energies from the SEAX method are obviously in better agreement with those

Table 1. The orbital energies of the U atom obtained with different methods (a.u.)

	ZORA[a]	IORA[b]	SEAX	Dirac-Slater[b]
$1s_{1/2}$	−4873.0	−4301.3	−4313.3	−4255.6
$2s_{1/2}$	−818.97	−795.37	−795.95	−795.01
$2p_{1/2}$	−789.88	−767.04	−767.74	−766.71
$2p_{3/2}$	−642.00	−626.19	−626.59	−625.96
$3s_{1/2}$	−202.63	−200.68	−200.74	−200.69
$3p_{1/2}$	−189.63	−187.82	−187.89	−187.82
$3p_{3/2}$	−156.71	−155.39	−155.43	−155.39
$3d_{3/2}$	−136.15	−134.99	−135.04	−134.99
$3d_{5/2}$	−129.47	−128.41	−128.41	−128.40
$4s_{1/2}$	−51.246	−51.089	−51.095	−51.092
$4p_{1/2}$	−45.427	−45.293	−45.303	−45.296
$4p_{3/2}$	−36.924	−36.823	−36.832	−36.826
$4d_{3/2}$	−27.664	−27.590	−27.595	−27.590
$4d_{5/2}$	−26.099	−26.032	−26.033	−26.032
$4f_{5/2}$	−13.913	−13.881	−13.879	−13.879
$4f_{7/2}$	−13.505	−13.472	−13.469	−13.472
$5s_{1/2}$	−11.333	−11.325	−11.327	−11.327
$5p_{1/2}$	−9.0768	−9.0722	−9.0744	−9.0735
$5p_{3/2}$	−7.0616	−7.0576	−7.0586	−7.0577
$5d_{3/2}$	−3.7671	−3.7645	−3.7650	−3.7644
$5d_{5/2}$	−3.4684	−3.4660	−3.4658	−3.4659
$6s_{1/2}$	−1.7190	−1.7197	−1.7197	−1.7198
$6p_{1/2}$	−1.0687	−1.0693	−1.0694	−1.0694
$6p_{3/2}$	−0.7410	−0.7410	−0.7410	−0.7410
$5f_{5/2}$	−0.1040	−0.1035	−0.1031	−0.1033
$5f_{7/2}$	−0.0735	−0.0729	−0.0724	−0.0728
$6d_{3/2}$	−0.0711	−0.0710	−0.0710	−0.0710
$6d_{5/2}$	−0.0538	−0.0537	−0.0537	−0.0537
$7s_{1/2}$	−0.1339	−0.1339	−0.1339	−0.1340

[a] Ref. [13]
[b] Ref. [19]

Table 2. The orbital energies of the Pu atom obtained with different methods (a.u.)

	ZORA	IORA	SEAX	Dirac-Slater
$1s_{1/2}$	−5175.0	−4537.8	−4552.1	−4485.8
$2s_{1/2}$	−871.66	−845.11	−845.91	−844.83
$2p_{1/2}$	−841.32	−815.60	−816.45	−815.25
$2p_{3/2}$	−676.22	−658.76	−659.24	−658.51
$3s_{1/2}$	−216.87	−214.65	−214.75	−214.69
$3p_{1/2}$	−203.29	−201.23	−201.33	−201.24
$3p_{3/2}$	−166.40	−164.91	−164.96	−164.92
$3d_{3/2}$	−145.11	−143.81	−143.86	−143.80
$3d_{5/2}$	−137.71	−136.52	−136.53	−136.52
$4s_{1/2}$	−55.464	−55.279	−55.295	−55.293
$4p_{1/2}$	−49.351	−49.192	−49.207	−49.200
$4p_{3/2}$	−39.724	−39.609	−39.617	−39.610
$4d_{3/2}$	−30.049	−29.962	−29.969	−29.963
$4d_{5/2}$	−28.299	−28.214	−28.213	−28.212
$4f_{5/2}$	−15.543	−15.502	−15.501	−15.502
$4f_{7/2}$	−15.076	−15.037	−15.032	−15.036
$5s_{1/2}$	−12.314	−12.306	−12.309	−12.310
$5p_{1/2}$	−9.9039	−9.8986	−9.9014	−9.9011
$5p_{3/2}$	−7.5618	−7.5569	−7.5583	−7.5573
$5d_{3/2}$	−4.0470	−4.0442	−4.0449	−4.0441
$5d_{5/2}$	−3.6992	−3.6966	−3.6965	−3.6964
$6s_{1/2}$	−1.7595	−1.7605	−1.7610	−1.7613
$6p_{1/2}$	−1.0681	−1.0689	−1.0692	−1.0693
$6p_{3/2}$	−0.7048	−0.7050	−0.7052	−0.7050
$5f_{5/2}$	−0.0556	−0.0550	−0.0548	−0.0549
$5f_{7/2}$	−0.0188	−0.0183	−0.0178	−0.0187
$6d_{3/2}$	−0.0329	−0.0361	−0.0362	−0.0361
$6d_{5/2}$	−0.0223	−0.0223	−0.0223	−0.0223
$7s_{1/2}$	−0.1223	−0.1224	−0.1224	−0.1224

from the 4-component Dirac-Slater calculations as compared with the result from the ZORA method.

Calculated result for molecules

In the molecular calculations, V_0 takes the form of Eq. (8) and V_N^A of atom A is chosen as that in Eq. (17). Equation (12) or (15) for atoms in average configurations is first solved with universal Gaussian basis sets to obtain atomic orbitals. The atomic orbitals are taken as basis sets extended with two STOs and one polarization functions for valence shells as in Ref. [32]. The local density approximation (LDA) with VWN correlation functional [34] is employed, and the gradient corrections for exchange due to Becke [35] and for correlation due to Perdew and Wang [36] are adopted. All matrix elements are evaluated by numerical integrations. The Becke partitioning scheme [37] is used for multicenter integrals. The Gauss-Chebeshev quadrature is used for radial integrals and Gauss-Legendre quadrature is used for angular integrals. The number of grid points is (100 × 80) for heavy elements and (80 × 60) for light elements. In bond energy calculations, the ground state energies of the constituent atoms are calculated using the same computational condition as that for the molecular calculation. The spin-polarized scheme is used for open shell atoms in scalar relativistic calculations, and the moment-polarized scheme [38, 39] is used in 2-component calculations. The calculated bond energies, bond lengths, and vibration frequencies by use of Eqs. (12) and (15) under LDA or GGA for a series of 2-atom molecules with closed shells are listed in Tables 3–6. The experimental and ZORA results are also listed in these tables for comparison. In ZORA calculations, the model potential is used in the kinetic operator [25, 32] and ESA [14] is adopted to eliminate the gauge dependency error. The results by 4-component relativistic DF calculations with BDF program [6] are also listed for comparison with the results of the 2-component SEAX calculations. The bond lengths, bond energies, and vibration frequencies are mainly determined by valence electrons; thus, the calculated results of these molecular constants are almost the same for the SEAX method and for the ZORA method with correction of the gauge dependency error. The results of scalar calculations agree quite well with the experimental results. The results of 2-component SEAX calculations agree very well with those from the 4-component relativistic DF calculations. The calculated bond lengths and vibration frequencies are in good agreement with experimental results, while there is still larger error in the calculated bond energies for some molecules which may be due to the error in the calculated ground state energies of the constituent atoms with open shells. In order to compare the performance of the ZORA and SEAX methods for the properties related to the inner shell electrons of heavy elements, the ionization energy of 4f electrons for Au atoms is calculated. The moment-restricted scheme and LDA are

Table 3. The bond lengths of scalar relativistic DF calculations (Å)

Compounds	Au_2	Ag_2	Cu_2	AuH	AgH	CuH	AuAg	AuCu	CuAg	AuF	AgF	CuF	AuCl	AgCl	CuCl	AuBr	AgBr	CuBr
Expt.	2.47	2.53	2.22	1.52	1.62	1.46	–	2.33	2.37	–	1.98	1.74	2.25	2.31	2.05	–	2.39	2.17
SEAX GGA	2.53	2.59	2.23	1.54	1.61	1.45	2.56	2.36	2.40	1.95	2.00	1.74	2.24	2.32	2.07	2.38	2.44	2.20
ZORA GGA	2.53	2.59	2.23	1.54	1.61	1.45	2.56	2.36	2.40	1.95	2.00	1.75	2.25	2.32	2.07	2.38	2.44	2.20
ZORA GGA[a,b]	2.52	2.56	2.21	1.54	1.62	1.45	2.54	2.34	2.38	1.95	2.01	1.74	2.24	2.31	2.05	2.37	–	–
SEAX LDA	2.47	2.51	2.27	1.53	1.59	1.44	2.49	2.30	2.33	1.91	1.94	1.71	2.19	2.26	2.02	2.32	2.38	2.15
ZORA LDA	2.47	2.51	2.27	1.53	1.59	1.44	2.49	2.30	2.33	1.91	1.94	1.71	2.19	2.26	2.02	2.32	2.38	2.15
ZORA LDA[a]	2.46	2.49	2.15	1.53	1.59	1.44	2.47	2.29	2.31									

[a] Ref. [14] for compounds Au_2–CuAg

[b] Refs. [24, 40] for compounds AuF–CuBr

Table 4. The bond energies of scalar relativistic DF calculations (eV)

Compounds	Au_2	Ag_2	Cu_2	AuH	AgH	CuH	AuAg	AuCu	CuAg	AuF	AgF	CuF	AuCl	AgCl	CuCl	AuBr	AgBr	CuBr
Expt.	2.31	1.66	2.05	3.36	2.39	2.85	2.08	2.39	1.76	3.0–3.7	3.67	4.46	3.5	3.24	3.96	–	3.1	3.43
SEAX GGA	2.22	1.65	2.13	3.26	2.48	2.98	2.08	2.39	1.87	3.39	3.65	4.47	2.95	3.04	3.64	2.66	2.64	3.25
ZORA GGA	2.21	1.65	2.13	3.26	2.46	2.98	2.08	2.39	1.87	3.39	3.65	4.47	2.95	3.04	3.64	2.65	2.64	3.25
ZORA GGA[a,b]	2.26	1.71	2.19	3.33	2.55	3.03	2.15	2.45	1.93	3.39	3.68	4.50	2.93	3.06	3.70	2.70	–	–
SEAX LDA	2.87	2.20	2.69	3.83	3.00	3.46	2.67	3.00	2.43	3.37	4.15	5.05	3.56	3.55	4.21	3.27	3.25	3.81
ZORA LDA	2.86	2.20	2.69	3.83	3.00	3.46	2.67	3.00	2.43	3.97	4.15	5.05	3.56	3.55	4.21	3.27	3.25	3.81
ZORA LDA[a]	2.92	2.28	2.77	3.78	2.95	3.43	2.76	3.09	2.51									

[a] Ref. [14] for compounds Au_2–CuAg

[b] Refs. [24, 40] for compounds AuF–CuBr

Table 5. The vibration frequencies of scalar relativistic DF calculations (cm^{-1})

Compounds	Au_2	Ag_2	Cu_2	AuH	AgH	CuH	AuAg	AuCu	CuAg	AuF	AgF	CuF	AuCl	AgCl	CuCl	AuBr	AgBr	CuBr
Expt.	191	192	265	2305	1760	1941	196	250	232	560	513	623	383	343	415	–	248	315
SEAX GGA	168	178	265	2262	1810	2009	178	238	221	540	482	615	358	315	393	241	230	303
ZORA GGA	167	178	265	2265	1811	2007	179	239	222	541	482	616	358	315	393	241	229	303
ZORA GGA[a,b]	174	183	272	2290	1810	2010	185	245	229	526	482	624	353	324	418	244	–	–
SEAX LDA	194	200	291	2325	1882	2047	202	261	246	588	543	671	391	350	428	268	252	329
ZORA LDA	192	198	291	2325	1889	2045	202	261	247	588	543	673	392	350	428	267	252	329
ZORA LDA[a]	193	206	298	2340	1890	2070	209	269	255									

[a] Ref. [14] for compounds Au_2–CuAg
[b] Refs. [24, 40] for compounds AuF–CuBr

Table 6. The result from 2-component SEAX calculations and 4-component relativistic DF calculations

Compounds	Au_2	AuCl	Bi_2	PbO	TlF	PbTe	TlCl
r_e(Å)							
Expt.	2.472	–	2.661	1.922	2.084	2.595	2.485
SEAX LDA	2.464	2.190	2.664	1.916	2.067	2.602	2.467
ZORA LDA	2.465	2.191	2.664	1.916	2.068	2.603	2.468
BDF LDA	2.463	2.188	2.645	1.915	2.067	2.602	2.465
SEAX GGA	2.522	2.241	2.691	1.944	2.113	2.649	2.530
ZORA GGA	2.523	2.241	2.692	1.944	2.113	2.649	2.530
BDF GGA	2.519	2.238	2.691	1.944	2.111	2.647	2.528
D_e(eV)							
Expt.	2.31	3.5	2.03	3.87	4.60	2.57	3.83
SEAX LDA	2.95	3.63	3.00	5.30	5.45	3.16	4.31
ZORA LDA	2.95	3.62	3.01	5.30	5.46	3.16	4.31
BDF LDA	2.96	3.64	3.01	5.30	5.46	3.16	4.32
SEAX GGA	2.29	3.00	2.43	4.66	4.98	2.58	3.89
ZORA GGA	2.29	3.00	2.43	4.66	4.98	2.58	3.89
BDF GGA	2.30	3.01	2.43	4.66	4.98	2.58	3.89
ω(cm^{-1})							
Expt.	191	383	173	721	477	212	284
SEAX LDA	199	409	180	–	491	210	307
ZORA LDA	199	409	179	758	492	211	307
BDF LDA	200	409	181	749	506	218	310
SEAX GGA	176	373	174	–	464	200	276
ZORA GGA	176	374	172	718	464	200	277
BDF GGA	178	370	175	717	461	194	268

Table 7. Ionization energies of the 4f electrons of Au atoms (eV)

No. of ionized electrons	ZORA	SEAX	BDF
1	95.41	95.21	95.22
2	220.58	220.16	220.11
3	378.63	377.94	377.77
4	572.31	571.34	570.95

adopted in the calculations. The 4-component relativistic DF calculations are also carried out with BDF program under the same conditions. The results are listed in Table 7. It can be seen that the result of SEAX calculations is in better agreement with that from the 4-component relativistic DF calculations as compared with the result obtained from the ZORA method.

Conclusion

A singularity excluded approximate expansion (SEAX) scheme is proposed to expand the total energy in relativistic density functional theory. The SEAX scheme provides a transition between the Breit-Pauli and RA expansions. The one-electron equation is derived variationally from the approximate total energy expression. The Hamiltonian of the one-electron equation is bounded from below; thus, the equation can be solved variationally. Comparing to the ZORA (MP) method, the gauge dependency error in ZORA method has been more completely eliminated in the SEAX method. The results of atomic calculations show that ZORA, IORA, and SEAX methods give very similar energies for the valence atomic orbitals, but the result by the SEAX method is obviously better than that by the ZORA method for the inner orbitals. For the deeper inner orbitals the result by IORA method is slightly better than that from the SEAX method, but compared with the SEAX method, the total energy and the one-electron equation is not connected variationally in the IORA method, and more computational efforts are demanded for solving the IORA equation because the metric matrix and the kinetic matrix need calculating in each cycle of iterations. The calculated orbital energies of U and

Pu by the SEAX method agree quite well with those obtained by solving the 4-component Dirac-Slater equation except for the 1s orbital. The calculations for a series of molecules show that for the molecular properties determined by valence electrons, the results of SEAX calculations are in good agreement with those from ZORA calculations with correction of the gauge dependency error, but for the properties related to the inner shells of heavy elements, the result given by the SEAX method is in better agreement with that by 4-component relativistic DF calculations as compared with the result from the ZORA method. The calculated results obtained by the two-component SEAX calculations agree very well with those from the 4-component relativistic DF calculations, while the computational efforts in the former method are much less than those in the latter.

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References

1. Balasubramniam K (1997) Relativistic effects in chemistry. Wiley, New York
2. Collins CL, Dyall KG, Schaefer III HF (1995) J Chem Phys 102: 2024
3. Visscher L, Saue T, Nieuwpoort WC, Faegri K, Crope O (1993) J Chem Phys 99: 6704
4. Visscher L, Lee TJ, Dyall KG (1996) J Chem Phys 105: 8769
5. de Jorg WA, Nieuwpoort WC (1996) Int J Quantum Chem 58: 203
6. Liu W, Hong G, Dai D, Li L, Dolg M (1997) Theor Chem Acc 96: 75
7. Kahn L, Baybutt P, Truhlar DG (1976) J Chem Phys 65: 3826
8. Dolg M, Stoll H (1996) In: Gschneider KA Jr, Eyring L (eds) Handbook on the physics and chemistry of rare earths, vol 22. Elsevier, Amsterdam, chap 152, p 607
9. Douglas M, Kroll NM (1974) Ann Phys (NY) 82: 89
10. Hess BA (1985) Phys Rev A32: 756; (1986) Phys Rev A33: 3742
11. Franke R, Kutzelnigg W (1992) Chem Phys Lett 199: 561
12. Chang Ch, Pelissier M, Duran Ph (1986) Phys Scr 34: 394
13. van Lenthe E, Baerends EJ, Snijders JG (1993) J Chem Phys 99: 4597
14. van Lenthe E, Baerends EJ, Snijders JG (1994) J Chem Phys 101: 9783
15. Dyall KG (1997) J Chem Phys 106: 9618; (1998) J Chem Phys 109: 4201
16. Dyall KG, Enevaldsen T (1999) J Chem Phys 111: 10000
17. Nakajima T, Hirao K (1999) Chem Phys Lett 302: 383
18. Nakajima T, Suzumura T, Hirao K (1999) Chem Phys Lett 304: 271
19. Dyall KG, van Lenthe E (1999) J Chem Phys 111: 1366
20. van Leeuwen R, van Lenthe E, Baerends EJ, Snijders JG (1994) J Chem Phys 101: 1272
21. van Lenthe E, van Leeuwen R, Baerends EJ, Snijders JG (1996) Int J Quantum Chem 57: 281
22. van Lenthe E, Snijders JG, Baerends EJ (1996) J Chem Phys 105: 6505
23. Philipsen PHT, van Lenthe E, Snijders JG, Baerends EJ (1997) Phys Rev B56: 13556
24. van Wüllen C (1998) J Chem Phys 109: 392
25. van Lenthe E, Ehlers A, Baerends EJ (1999) J Chem Phys 110: 8943
26. Wang F, Li L (2000) Acta Chimica Sinica 12: 1499
27. Kutzelnigg W (1997) Chem Phys 225: 203
28. Ishikawa Y, Baretty R, Binning RC Jr (1985) Chem Phys Lett 121: 130
29. Stanton RE, Havriliak SJ (1984) J Chem Phys 81: 1910
30. Kellö V, Sadlej AJ (1998) Int J Quantum Chem 68: 159
31. Barysz M, Sadlej AJ (1997) Theor Chem Acc 97: 260
32. Wang F, Hong G, Li L (2000) Chem Phys Lett 316: 318
33. de Castro EVD, Jorge FE (1998) J Chem Phys 108: 5225
34. Perdew JP, Wang Y (1992) Phys Rev B45: 13244
35. Becke AD (1988) Phys Rev A38: 3098
36. Perdew JP, Wang Y (1986) Phys Rev B33: 8800
37. Becke AD (1988) J Chem Phys 88: 2547
38. Ellis DE, Goodman GL (1984) Int J Quantum Chem 25: 185
39. Liu W, Küchle W, Dolg M (1998) Phys Rev A58: 1103
40. Liu W, van Wüllen C (1999) J Chem Phys 110: 3730