

Four-component relativistic density functional calculations of heavy diatomic molecules

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We perform accurate four-component calculations for heavy closed-shell diatomic molecules in the framework of relativistic density functional theory using local and gradient corrected density functional schemes. As examples we have chosen Cu_2 , Ag_2 , Au_2 , Tl_2 , Pb_2 , Bi_2 , and Pt_2 . The potential energy curves show the quality, and the discrepancies of the density functionals unscreened from any approximation of the relativistic effects. © 2000 American Institute of Physics. [S0021-9606(00)31105-9]

I. INTRODUCTION

Besides a large number of nonrelativistic calculations of diatomic molecules, several calculations exist where relativistic effects are taken into account in various approximations. An older review is given in the book by Mulliken and Ermler,¹ whereas the books of Balasubramanian^{2,3} reviews nonrelativistic as well as relativistic results especially for diatomic molecules. An experimental review on mainly diatomic molecules is given by Morse in Ref. 4.

From a general point of view, it is clear that only four-component relativistic calculations in combination with large multiconfiguration Dirac–Fock (MCDF-), configuration interaction, coupled cluster- or sophisticated density functional procedures will lead to good results in molecular calculations.

Reviewing the literature for molecular calculations considering relativistic effects in different kind of approximations, one can roughly classify them into two groups. In the first group more effort is put into the correlation part, whereas a good description of the relativistic effects is being undertaken in the second group.

There are a large number of calculations in which the relativistic effects are just incorporated via relativistic effective core potentials. Schwerdtfeger⁵ and Danovich *et al.*⁶ then proceed with correlation calculations up to the quasi-relativistic CI with singles and doubles (triples) [QCISD(T)] level. GAUSSIAN 92 calculations with correlation on the MP2 level are done by Glukhovtsev *et al.*,⁷ where again pseudopotentials are used to include the relativistic effects; here, spin-orbit corrections are at least added perturbatively. The

most extensive work in this respect has been done by Balasubramanian and co-workers, who also use effective core potentials but spin-orbit integrals are partially taken into account and a CI calculation is added using different outermost wave functions. A good review of their procedure, as well as others to handle relativistic effects in molecular calculations, can also be found in the book by Balasubramanian.² Examples which fit in this discussion here are Refs. 8–10. A purely perturbative approach for the relativistic effects using the Cowan–Griffith operator is used by Kello *et al.*,¹¹ who do calculations on heavy elements-hydrides with MBPT for the correlation. Here, no spin-orbit effects are included. The same is true for a one-component relativistic calculation based on the Douglas–Kroll transformation of Kaldor and Hess,¹² who apply a sophisticated coupled-cluster approach to AuH.

To the second group belongs the work of Matsuoka,¹³ who does a full Dirac–Fock calculation for linear molecules, respectively, Dirac–Fock–Roothaan calculations plus an additional density functional calculation to account for the correlation part.¹⁴ With a four-component Dirac–Fock method, Dyll *et al.*^{15,16} have clearly demonstrated the influence of relativistic effects on the energy eigenvalues as well as the wave functions in molecular calculations. Recent fully relativistic CI results on diatomic molecules exist from Quiney *et al.*, as well as¹⁷ Dirac–Fock–CCSD coupled-cluster single double calculations from de Jong *et al.*^{18,19}

A promising and widely used alternative to calculate ground-state properties is offered by relativistic density functional theory (RDFT), which includes both relativistic and correlation effects. Very extensive studies of relativistic effects on molecules have been done by the Amsterdam group by van Lenthe *et al.*²⁰ Within their zeroth-order regular approximation (ZORA) method,²¹ in which relativity is taken into account partially concerning the treatment of the kinetic

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energy, they discuss the influence of spin-orbit splitting in closed-shell diatomic molecules. We further mention the work of Mayer *et al.*,²² which is based on the additional approximation of neglecting the spin-orbit coupling. This is often called the scalar relativistic approximation. They mainly focus on gold clusters and gold compounds. Because in the element gold the outer 6s electron is strongly influenced by relativistic effects but does not exhibit spin-orbit splitting, their method is appropriate and works well.²³ (An up-to-date review of the various methods of relativistic descriptions of molecules can be found in Ref. 2 and results in Ref. 3.)

In this paper, we go one step further; we use a four-component relativistic molecular description with the newest form of the relativistic density functionals.^{41,24,25} We apply this method to heavy diatomic molecules and compare them to previous results. We have chosen Au₂ and the homologues Ag₂ and Cu₂ as molecules which are governed by the last s-electron, Tl₂, Pb₂, and Bi₂, whose binding mainly results from the last p-electrons, which are strongly influenced by relativistic effects (especially spin-orbit splitting) and Pt₂ as an example of a d-element.

Our work represents the first density functional calculations where relativity is completely taken into account so that the discrepancies with respect to the experimental results can be fully credited to the approximation of the density functionals.

We briefly outline our method in Sec. II. In Sec. III we discuss the computational details. We apply this method to the heavy diatomic molecules mentioned above and discuss and compare the results with other calculations in Sec. IV. Finally, in Sec. V we give a summary and conclusions.

II. METHOD

Our method is based on the RDFT, which may be systematically derived from quantum electrodynamics.^{26–28} Neglecting the minorly important contributions from the spatial components of the four current $j^\nu(\mathbf{r}) = (j^0, \mathbf{j})$, the basic ingredient of RDFT is the single-particle density $n(\mathbf{r}) = j^0$, which may be expressed by a set of N discrete four-component auxiliary orbitals $\psi_k(\mathbf{r})$

$$n(\mathbf{r}) = \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \psi_k^\dagger(\mathbf{r}) \psi_k(\mathbf{r}), \quad (1)$$

where we have restricted ourselves to the no-pair approximation. The total energy may then be written as

$$E[n] = T_s + E_{\text{ext}}[n] + E_H[n] + E_{\text{xc}}[n]. \quad (2)$$

Here, the first term is the kinetic energy (we use atomic units throughout),

$$T_s = \sum_{-mc^2 < \epsilon_k \leq \epsilon_F} \int d^3r \psi_k^\dagger(\mathbf{r}) \times [-i\mathbf{c}\boldsymbol{\alpha} \cdot \nabla + (\beta - 1)mc^2] \psi_k(\mathbf{r}), \quad (3)$$

the second is the interaction energy of the electrons with the nuclei, the third the direct electron–electron interaction energy, and the last term the exchange–correlation energy. Us-

ing the representation of the density (1) the total energy can be calculated by solving the relativistic Kohn–Sham equations

$$(-i\mathbf{c}\boldsymbol{\alpha} \cdot \nabla + (\beta - 1)mc^2) \psi_k + v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \psi_k = \epsilon_k \psi_k, \quad (4)$$

with the interaction potential of the electrons with the nuclear charges Z_α ,

$$v_{\text{ext}}(\mathbf{r}) = - \sum_\alpha \frac{Z_\alpha e^2}{|\mathbf{R}_\alpha - \mathbf{r}|}, \quad (5)$$

the Hartree potential

$$v_H(\mathbf{r}) = e^2 \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad (6)$$

and the exchange–correlation potential

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}[n]}{\delta n(\mathbf{r})}. \quad (7)$$

In our work we apply the relativistic local density approximation (RLDA) for E_{xc} (utilizing the Vosko–Wilk–Nusair parametrization²⁹ for correlation) to achieve self-consistency. Nonlocal corrections, for which the relativistic form (RGGGA)²⁵ of Becke’s generalized gradient approximation (GGA) for exchange (B88)³⁰ and the Perdew (P86)³¹ functional for correlation is used, are then evaluated perturbatively.

In our linear combination of atomic orbitals (LCAO) approach the molecular wave functions $\psi_k^{\text{MO}}(\mathbf{r})$ are expanded in four-component relativistic atomic Dirac spinors $\xi_\mu^{n\kappa m}(\mathbf{r})$

$$\psi_k^{\text{MO}}(\mathbf{r}) = \sum_{\mu n \kappa m} c_{k\mu}^{n\kappa m} \xi_\mu^{n\kappa m}(\mathbf{r}); \quad (8)$$

$$\xi_\mu^{n\kappa m}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} f_\mu^{n\kappa}(r) \mathcal{Y}_\kappa^m(\Omega) \\ i g_\mu^{n\kappa}(r) \mathcal{Y}_{-\kappa}^m(\Omega) \end{pmatrix}.$$

The superscripts n , κ , m denote the main-, the Dirac- and the (half-integer) magnetic quantum number, respectively. All matrix elements are computed numerically on a three-dimensional point mesh with the very accurate multicenter integration scheme of te Velde and Baerends.³² Details of the molecular calculations can also be found in Refs. 33–35.

III. COMPUTATIONAL DETAILS

As already discussed in our previous publication,³⁵ we have included all relativistic corrections resulting from the kinematics of the electrons (Dirac kinetic energy) and the photons (retarded Breit corrections to the Hartree and exchange energy). On the other hand, we have neglected all typical quantum electrodynamical effects, i.e., all consequences of the creation of virtual electron–positron pairs (compare the discussion in Ref. 28), as well as the corrections due to the finite nuclear size.

Concerning the Breit corrections, it seems necessary to emphasize that for the dimers considered here the spatial components of the four-current (1) vanish (due to the closed-shell structure). As a consequence, there are no Breit contri-

butions to the Hartree energy and potential. However, this does not imply that the corresponding contributions to the exchange-correlation functional vanish as well. In fact, the xc functionals used in our work contain Breit corrections. In order to check their impact on the molecular results, we have performed a calculation for the gold dimer with the transverse component of E_{xc} explicitly set to zero. This results in a difference of 0.04 eV in the RLDA binding energy (at an internuclear separation of 4.7 a.u.—the equilibrium distance). For the gold atom, on the other hand, the transverse Hartree energy does not vanish. Its absolute size of 0.25^*10^{*-6} a.u., however, is marginal, so we have neglected this contribution throughout.

Concerning the electro-dynamical effects, it was pointed out in a systematic study by Pyykkö and Labzowsky³⁶ that their impact on the valence orbital energy (as a measure of the ionization potential) of gold amounts to only 1%–2% of the kinematic relativistic correction, i.e., 0.05 eV in absolute numbers. One would expect them to be similarly small for molecular binding properties. They are even smaller for the lighter elements considered in our work, of course.

Furthermore, as it was shown by the same authors and also by Mayer *et al.*,²² the introduction of extended nuclei in molecular structure calculations has no significant impact on the molecular properties.

Consequently, in view of the overall level of accuracy of 0.1 eV at which we aim and compared with the remaining uncertainties in the presently available xc functionals, the omission of electro-dynamical and finite nuclear size effects seems highly justified.

One of the major problems in all our calculations until now was the computation of the Hartree potential, which was treated in an optimized monopole approximation.^{37,33} We now have improved this approximation. Also, dipole and quadrupole parts of the Hartree potential are taken into account, which is correct for systems up to open *s*, *p*, and *d* shells. Details of the actual formulation are given in the Appendix.

The basis sets which we use in our calculations may be divided into two parts, a minimal basis set and an extended basis. The first one consists of all occupied four-component wave functions of the neutral atoms. As an example, for gold the minimal basis set is defined as $1s_{1/2}$ to $6s_{1/2}$. In a first step, we calculate the total energy curve with this minimal basis set. To be more complete in the molecular calculations, we proceed as follows: At a fixed internuclear separation (minimum of the total energy), which is observed by the minimal basis-set calculation, we successively add basis functions of the next few unoccupied orbitals from ionized atoms. In this second step, we perform molecular calculations at this fixed internuclear distance with each of these new basis functions until we find the minimum of the total energy as function of the degree of ionization, which shifts these additional orbitals towards the molecular binding region. This procedure is continued with the next additional atomic function until no change in the total energy is observed anymore. The degree of ionization lies typically in the range of +2 to +10. In all practical cases here, the addition of further unoccupied $p_{1/2}$, $p_{3/2}$, $d_{3/2}$, $d_{5/2}$, and $f_{5/2}$, $f_{7/2}$,

wave functions was sufficient. For the coinage metals and platinum we have used, the $(1s-n_s)$ wave functions as a minimal set and the $n(p_{1/2}, p_{3/2}, d_{3/2}, d_{5/2})$ wave functions as an extended basis set ($n=4,5,6$ for Cu, Ag, Pt, and Au, respectively). In the case of Tl_2 , Pb_2 , and Bi_2 , the minimal set consists of the occupied atomic $(1s-6p)$ wave functions, while the extended basis was constructed by slightly ionized $6d$ and $5f$ wave functions. In order to check the completeness of the basis, we have added, in the case of the gold dimer, the $5f(f_{5/2}, f_{7/2})$ wave functions to the optimized basis set. We observed no change in the total energy compared with the extended $(6p, 6d)$ basis. Finally, we have recalculated the complete total energy curves with this optimized basis set.

In all our molecular calculations, we use the RLDA in the self-consistent solution of the Kohn-Sham equations (4) and then add in the gradient correction as a perturbation. This procedure saves a lot of time because one does not need to calculate the second derivatives of the density. And, most important, it does not lead to a considerable error because the difference between a full self-consistent field (SCF) calculation including the RGGGA correction and a perturbative treatment is very small (less than 0.01 eV), as already pointed out by Mayer *et al.*²² and van Lenthe *et al.*²⁰

To obtain the molecular binding energies, we have to subtract the total energies of all atomic species in the molecule. This is done either via a direct molecular calculation at large internuclear distances or directly from separate atomic calculations in their ground states. Of course, we are well aware of the fact that not for every case do these atomic calculations lead to the correct physical value. Due to the density functional approach, one arrives at the average of the multiplet energy of the atom and not at the true ground state which is the reference in every experimental value. Thus, we perform in principle the same procedure which was described in detail by van Lenthe *et al.*²⁰ in their paper. But, in contrast to them we are in a better position because we arrive at our four-component relativistic calculations at the *jj*-coupled atomic ground states. Luckily enough, for the molecules which we are calculating here we only have to use this level-averaging procedure in the case of Pt_2 , where the correction is just 0.04 eV for one Pt atom. In all other cases we automatically converge to the atomic ground state in *jj* coupling. Finally, we remark that our atomic ground-state energies have been evaluated with the same purely density-dependent approximations for E_{xc} used in the molecular calculations, thus neglecting the current contributions to E_{xc} . However, while the spatial components of j^p vanish for the dimers considered here, the unpaired valence *s*-electron leads to a nonzero three-current in the case of the Ib elements, reflecting the electron's spin. In nonrelativistic DFT this spin is usually taken into account via the spin-density dependent forms of the LDA or GGA which lower the atomic ground-state energy. Unfortunately, no current-dependent relativistic generalizations of these functionals are available (apart from the LDA exchange), so we have neglected *j*. As a consequence, our atomic ground-state energies are somewhat higher than the energies corrected for this spin/current contribution, so that the corresponding dissociation energies are

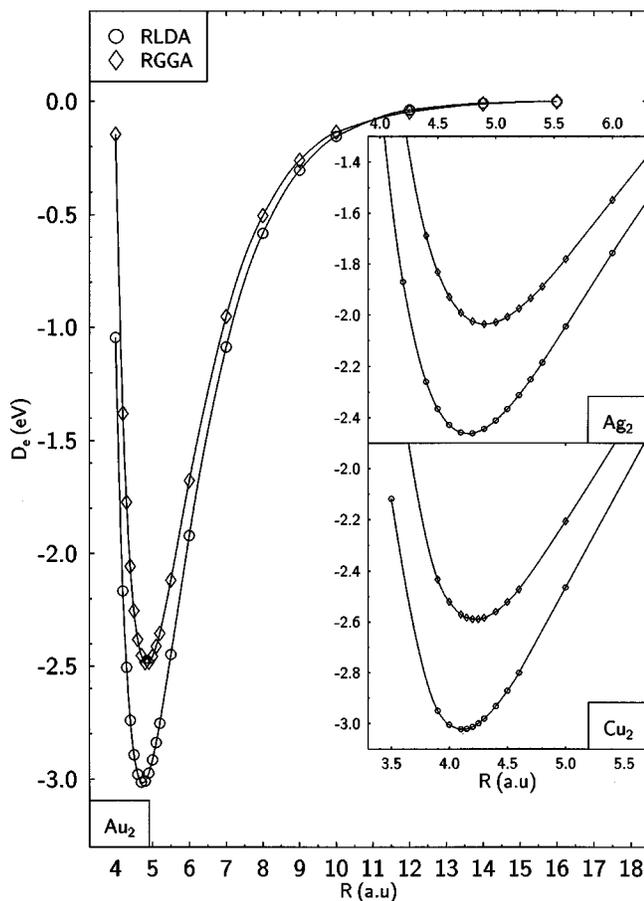


FIG. 1. The potential energy curves of the three diatomic molecules Cu_2 , Ag_2 , and Au_2 from our four-component relativistic density functional calculation in the RLDA and RGGA approximation.

slightly overestimated (compare Ref. 35). It should be emphasized, on the other hand, that the values for the equilibrium distances and frequencies are not affected by the treatment of the atomic reference energy. Work concerning this point is in progress.

IV. RESULTS AND DISCUSSION

Using the procedure described in Secs. II and III, we have calculated the various closed-shell diatomic molecules of heavy elements mentioned above. In Fig. 1 we present the potential energy curves for the Ib-element diatomic molecules Cu_2 , Ag_2 , and Au_2 . For every molecule the lower of the corresponding curves shows the RLDA results and the upper are our final RGGA result, respectively. Figure 2 shows the potential energy curves for Tl_2 , Pb_2 , and Bi_2 . In order not to complicate these figures, we do not include here the nonrelativistic curves, which were already discussed in the literature for all of these diatomic molecules.^{38,39,5,37} The direct relativistic effect was smallest for Cu_2 with 1 eV, whereas it was nearly 2.5 eV for Bi_2 .

At first, one clearly can see in both figures that the potential energy curves go to zero for very large internuclear distances, not only for the 6s-electron bound system Au_2 but also, e.g., for the $6p^3$ -electron molecule Bi_2 , as discussed above. The potential energy curve for Au_2 is very smooth,

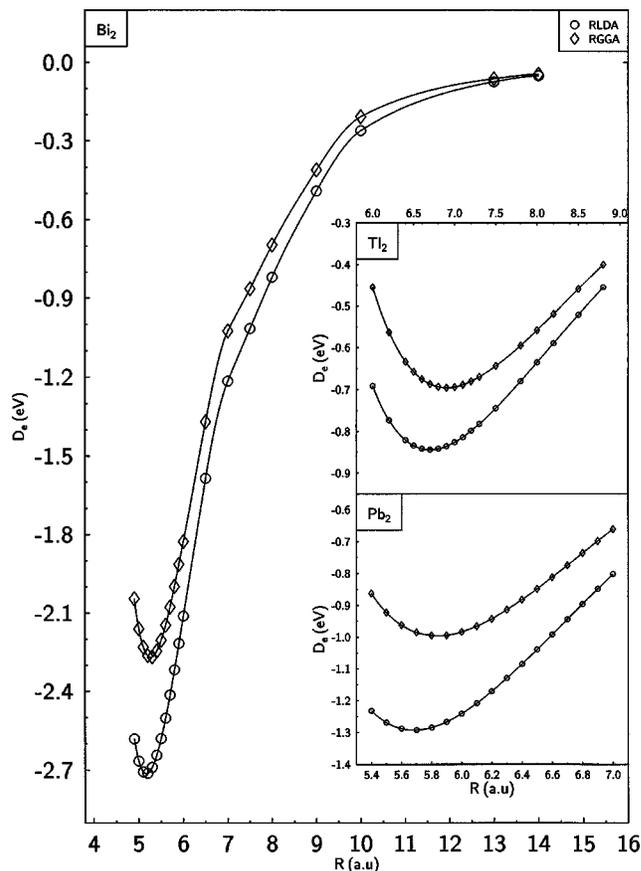


FIG. 2. The potential energy curves of the three diatomic molecules Tl_2 , Pb_2 , and Bi_2 from our four-component relativistic density functional calculation in the RLDA and RGGA approximation.

whereas the Bi_2 potential energy curve has two kinks, the first at about 6.7 a.u. and the second around 9 to 10 a.u. This may be due to an avoided crossing with another state which in jj coupling can be constructed from $6p_{1/2}^2 6p_{3/2}^1$ with the same total angular momentum as the ground state; at about 9 to 10 a.u. they cross again. This behavior is nearly in full accordance with Fig. 2 in Ref. 9.

To see the contributions from the RGGA correction, we also present the RLDA potential energy curves without the gradient correction in both figures. It should be noted here also that for the diatomic molecules which are dominantly bound by the s -electrons the total energy has non-negligible components from the dipole and quadrupole potential terms which are now included in our calculations and which were missing in our last publication.³⁵ This contribution arises mainly from the lower-lying d -orbitals which in the molecular calculation are not fully occupied anymore. This leads to a change in the potential energy curve of 0.4 eV for Cu_2 to 0.6 eV for Au_2 . For the d -electron bound molecule Pt_2 , this effect is already 1 eV, but for the $6p$ -element dimers it is only 0.15 to 0.3 eV. A more detailed discussion about the quality of the multipolar expansion is given at the end of the Appendix.

As can be seen in Figs. 1 and 2, the GGA contribution shifts the minimum of the potential energy curves to larger internuclear separations, but improves the bond energy considerably. The results for the spectroscopic constants of the

TABLE I. Bond energies and bond lengths of the lb-element diatomic molecules Cu₂, Ag₂, and Au₂ in comparison to some results of other relativistic calculations as well as the experimental values.

Mol.	Ref.	Method ^a	R_e (a.u.)	D_e (eV)	ω (cm ⁻¹)
Cu ₂	40	ZORA-GGA	4.18	2.19	272
	this work	4-comp. RGGGA	4.23	2.59	263
	4	exp.	4.19	2.01±0.08	266
Ag ₂	42	MP2	4.72	2.1	214
	40	ZORA-GGA	4.84	1.71	183
	this work	4-comp. RGGGA	4.91	2.02	181
		exp.	4.79 ^b	1.65±0.03 ^c	192 ^d
Au ₂	47	CASSCF-MRSDCI		2.0	
	5	QCISD(T)	4.80	1.99	
	40	ZORA-GGA	4.76	2.26	174
	20	ZORA-GGA	4.75	2.31	178
	this work	4-comp. RGGGA	4.88	2.50	169
48	exp.	4.67	2.29±0.02 ^e	191	

^aThe explanations of the abbreviations are found in the references.

^bReference 43.

^cReference 44.

^dReference 45.

^eReference 46.

coinage metal dimers Cu₂, Ag₂, and Au₂ are summarized in Table I. This table also includes the full original information concerning the experimental values with error bars. We compare our new results with a few representative relativistic calculations of other authors as well as the experiment. Due to the fact that our calculations handle the relativistic part correctly, we should expect that our results fit the experimental values best. But, this is not the case. The results of van Lenthe^{40,20} are closer to the experiment, although their ZORA-GGA method still uses a number of approximations in the treatment of the relativistic effects. On the other hand, the density functionals used are identical, B88 for the exchange and P86 for correlation. Of course the discrepancies are not too big, but our values for the bond length are consistently too large with an increasing trend towards the heavier elements. On the other hand, the binding energies are too strong with an decreasing trend for heavier elements.

The same general trend can also be seen in Table II, which summarizes the results for four elements in the same row in the periodic table: Tl₂, Pb₂, Bi₂, and Pt₂. The first three 6*p*-elements are dominated by relativistic effects including the spin-orbit splitting, whereas Pt₂ should be only moderately relativistic. (The first three were also studied in an earlier work.³⁴) Due to relatively large error bars and different values in the experimental data, all four diatomic molecules show reasonably good agreement for the bond energies. But again, the bond length is always slightly overestimated. An exception is Tl₂, whose bond length is largely overestimated, but this can be understood due to the very weak binding and flat potential energy curve of this molecule. In addition, one should have in mind that the experimental values for this molecule are not known accurately at all. Again, the result of van Lenthe for Bi₂ is astonishingly accurate, whereas the other theoretical predictions have discrepancies similar to our results.

This unexpected behavior that our results are not as good

TABLE II. Bond energies and bond lengths of the diatomic molecules Tl₂, Pb₂, Bi₂, and Pt₂ in comparison to some results of other relativistic calculations as well as the experimental values.

Mol.	Ref.	Method ^a	R_e (a.u.)	D_e (eV)	ω (cm ⁻¹)
Tl ₂	49	REP MC-SCF	6.69	0.37	39
	this work	4-comp. RGGGA	6.88	0.70	61
	50	exp.	≈5.7	0.43±0.04	78
	51	exp.	(5.2)	0.63±0.15	136
Pb ₂	52	REP-RCI	5.61	0.88	103
	this work	4-comp. RGGGA	5.83	1.00	100
	53	exp.	5.54 ^b	≈1.0	110 ^b
	54	exp.		0.82±0.06	119
Bi ₂	9	CASSCF-FOCI	5.22	1.88	151
	20	2-comp. DFT	5.07	1.98	174
	this work	4-comp. RGGGA	5.27	2.26	142
	55	exp.	5.03	2.04	173
Pt ₂	10	CASSCF-FOCI	4.64	≈2.0	189
	this work	4-comp. RGGGA	4.52	3.94	234
	57	exp.	(4.42) ^c	3.71	259
		exp.		3.14±0.02 ^d	217 ^e

^aThe explanations of the abbreviations are found in the references.

^bReference 56.

^cAssumption in Reference 57.

^dReference 58.

^eReference 59.

as the results of van Lenthe *et al.*²⁰ can only be understood in the way that the omission of parts of the relativistic effects in their ZORA approximation just cancels at least parts of the errors which still are present in the density functionals. These were used identically in their calculations, as well as in ours. We, on the other hand, use a relativistic four-component all-electron method. Here, all of the direct and indirect relativistic effects including spin-orbit splitting are included. In addition, we should mention that we do not need any type of atomic corrections for the atoms calculated here (besides Pt), as was explained in Sec. III. Because of the general quality of the relativistic treatment in our calculations, we are sure that in our results we finally directly see the deficiencies of the GGAs of Becke³⁰ and Perdew,³¹ which are frequently used in DFT calculations nowadays (Refs. 20 and 22 as examples), but which were screened by the partial neglect of relativistic effects up to now. Thus, an improvement of the density functionals seems to be essential.

V. SUMMARY AND CONCLUSION

In this paper we have presented the first results for the calculation of potential energy curves for heavy diatomic molecules in a four-component relativistic density functional approach. The exchange and correlation contributions were approximated using the best known relativistic density functionals. The resulting binding energies still show a few tenths of an eV discrepancy compared to the experimental values. The bond distances calculated with the RGGGA come out 1% to 5% larger (with the exception of Tl₂) than for the RLDA. We believe that it is essential to perform this kind of four-component calculation because the relativistic effects strongly increase for even heavier elements. Not only does the spin-orbit coupling split the single-particle energies but

the radial parts of the large and small components of the four spinors also show an increasingly different radial and angular behavior, which in turn influences the other wave functions due to self-consistent effects. If these effects are not taken into account in a correct way, one will not obtain good results for molecules with heavier constituents. This statement is probably already true for the three $6p$ -element diatomic molecules which we have calculated here.

Of course, we are well aware that correlation effects would be handled better within a full CI treatment, which then also allows as to calculate excited states for spectroscopic purposes. Both effects are equally important in the region of the $6p$ -elements, but relativistic effects become much stronger for even heavier elements. So, all the effort should be invested in bringing both methods together.

The results presented in this paper shows the quality/deficiency of the density functional approximations unscreened from any kind of relativistic approximations. This could be a guide for the development of better density functionals.

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APPENDIX

In this section we describe our improved calculation scheme for the Hartree potential. The Hartree energy $E_H[n]$ can be written as

$$\begin{aligned} E_H[n] &= \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &= \frac{1}{2} \int d^3r n(\mathbf{r}) v_H(\mathbf{r}). \end{aligned} \quad (\text{A1})$$

Here, the Hartree potential is given by

$$v_H(\mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (\text{A2})$$

Since we use a numerical 3D integration procedure, the computation of (A2) would be too time consuming. To avoid this problem and nevertheless calculate $v_H(\mathbf{r})$ with sufficient accuracy, several suggestions have been made.^{60,61} The basic idea is to introduce an auxiliary density $\tilde{n}(\mathbf{r})$, which fits the ‘‘true’’ density $n(\mathbf{r})$, Eq. (1), and allows one to simplify the calculation of the Hartree potential

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \Delta n(\mathbf{r}) \rightarrow v_H(\mathbf{r}) = \tilde{v}_H(\mathbf{r}) + \Delta v_H(\mathbf{r}). \quad (\text{A3})$$

From a general point of view, no special assumptions about the origin of the auxiliary density have to be made. Usually it is convenient to obtain this density $\tilde{n}(\mathbf{r})$ by a least-square fit to the true density $n(\mathbf{r})$,

$$\int d^3r (n(\mathbf{r}) - \tilde{n}(\mathbf{r}))^2 = \int d^3r \Delta n(\mathbf{r}) \Delta n(\mathbf{r}) = \min. \quad (\text{A4})$$

An alternative scheme was proposed by Dunlap *et al.*⁶⁰ Insertion of $n(\mathbf{r})$ and $v_H(\mathbf{r})$ into Eq. (A1) gives

$$\begin{aligned} E_H[n] &= E_H[\tilde{n}, \Delta n] \\ &= \int d^3r n(\mathbf{r}) \tilde{v}_H(\mathbf{r}) - \frac{1}{2} \int d^3r \tilde{n}(\mathbf{r}) \tilde{v}_H(\mathbf{r}) \\ &\quad + \underbrace{\frac{1}{2} \int d^3r \int d^3r' \frac{\Delta n(\mathbf{r}) \Delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{E_H^I(\Delta n(\mathbf{r}))}, \end{aligned} \quad (\text{A5})$$

Here, the last term E_H^I represents the self-interaction energy of the difference density $\Delta n(\mathbf{r})$, which is of second order in $\Delta n(\mathbf{r})$. Of course, omission of this term would lead to an error in the total energy. However, one can minimize this error by requiring

$$E_H^I(\Delta n(\mathbf{r})) = \frac{1}{2} \int d^3r \Delta n(\mathbf{r}) \Delta v_H(\mathbf{r}) = \min. \quad (\text{A6})$$

Before proceeding, we specify the nature of the auxiliary density \tilde{n} . In a multipolar expansion, we make the ansatz

$$\begin{aligned} \tilde{n}(\mathbf{r}) &= \sum_i^{N_{\text{atom}}} \sum_j^{M_j} \sum_{l=0}^{L_j} \sum_{m=-l}^{m=l} Q_{jm}^{il} f_j^i(r_i) Y_{lm}(\Omega_i) \\ &=: \sum_k q_k g_k(\mathbf{r}). \end{aligned} \quad (\text{A7})$$

Here, i runs over all atoms (symmetry equivalent centers), f_j^i represents the j th basis function of the center i [i.e., the absolute squares of the radial parts of the atomic wave functions $f^{n\kappa}, g^{n\kappa}$ of (8)] and runs over all orbitals of interest. The $Y_{lm}(\Omega)$ are the spherical harmonics. The coefficients Q_{jm}^{il} (or the q_k in a simpler form) may be considered as ‘‘occupation numbers.’’ After insertion of (A7) into (A6) and minimization with respect to the coefficients q_k , we obtain the following linear system of equations:

$$\langle n | g_p \rangle = \sum_k q_k \langle g_p | v_k \rangle. \quad (\text{A8})$$

where p, k run over all basis fit functions. Here, v_k denotes the potential function

$$v_k(\mathbf{r}) = \int d^3r' \frac{g_k(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (\text{A9})$$

In addition, the auxiliary density should conserve the total charge of the molecule

$$N_{\text{el}} = \sum_k q_k \int g_k(\mathbf{r}) d^3r. \quad (\text{A10})$$

This constraint is introduced in (A8) by a Lagrange factor λ . In a more compact form, we can write for (A8)

$$b_p = \sum_k q_k A_{pk} - \lambda \int g_k(\mathbf{r}) d^3r, \quad (\text{A11})$$

where $b_p := \langle n | g_p \rangle$ and $A_{pk} := \langle g_p | v_k \rangle$ on the right-hand side of Eq. (A8). As a result, from (A11) we obtain the occupations (fit coefficients) q_k and thus the auxiliary density (A7). The Hartree potential $\tilde{v}_H(\mathbf{r})$ is determined by insertion of (A7) into the standard one center multipolar expansion formula

$$\tilde{v}_H(\mathbf{r}) = \sum_{ijlm} Q_{jm}^{il} \frac{4\pi}{2l+1} \frac{1}{r_i^{l+1}} Y_{lm}(\Omega_i) \left[\int_0^{r_i} dr' r'^l f_j^i(r') + r_i^{2l+1} \int_{r_i}^{\infty} dr' \frac{1}{r'^{l+1}} f_j^i(r') \right]. \quad (\text{A12})$$

Despite the fact that we do not explicitly evaluate the self energy E_H^{II} , this term is used by (A6) to determine the Hartree potential as well as possible. That means that the error induced by the omission of E_H^{II} in the total energy calculation is minimized.

However, an accurate Hartree potential depends on the ansatz (A7), i.e., which type of functions are taken into account. Up to now we only used monopole-type functions. As an example, for the Au_2 molecule the radial wave functions $1s_{1/2}$ to $6s_{1/2}$ of neutral atoms, which define a minimal basis set and in addition the $6p_{1/2,3/2}$ and $6d_{3/2,5/2}$ basis functions of slightly ionized atoms were taken into account in the monopole part of the multipolar expansion ($L_j=0$). In this work we extend our method. For all np and nd functions in (A7) the dipole and quadrupole parts are calculated, respectively. In contrast to former implementations, in which well-defined but mesh-dependent fit functions were used,⁶¹ we consider our atomic basis functions to be more physical and therefore appropriate for a multipolar expansion. In addition, the p and d functions can be determined in such a way that they reproduce the multipolar moments of the molecular charge density. This can be taken into account as a further constraint in (A8). Unfortunately, multipoles higher than quadrupoles are currently not available.

In order to check whether the angular momentum expansion (A12) for the Hartree potential is converged, we have analyzed the dependence of the dissociation energy on the maximum angular momentum L_H in the expansion. In the following we consider Ag_2 , Au_2 , and Bi_2 in more detail. For the full orbital basis (including d -states in the case of Au and Ag, f -states for Bi) we have, starting with the monopole term ($L_H=0$), successively switched on the dipole ($L_H=1$) and quadrupole ($L_H=2$) components of the Hartree potential and performed molecular calculations near the equilibrium distance. The resulting binding energies are presented in Table III. For Ag_2 and Bi_2 no significant changes in the binding energy are observed when going from the dipole to the quad-

TABLE III. Values for the RLDA binding energy (eV) for the molecules Ag_2 , Au_2 , and Bi_2 for a fixed internuclear separation near the equilibrium distance in dependence of the multipolar expansion of the Hartree potential.

	Ag_2	Au_2	Bi_2
$L_H=0$	-2.84	-3.65	-2.98
$L_H=1$	-2.47	-3.25	-2.80
$L_H=2$	-2.45	-3.01	-2.79

TABLE IV. Atomic RLDA valence energy eigenvalues (eV) for Ag_2 , Au_2 , and Bi_2 .

	Ag_2		Au_2		Bi_2
					$5d_{5/2}$ -25.17
$4d_{3/2}$	-8.02	$5d_{3/2}$	-8.10	$6s_{1/2}$	-14.06
$4d_{5/2}$	-7.46	$5d_{5/2}$	-6.57	$6p_{1/2}$	-5.77
$5s_{1/2}$	-4.69	$6s_{1/2}$	-6.06	$6p_{3/2}$	-3.89

ruple expansion, explicitly indicating convergence of the multipole expansion. On the other hand, convergence is not obvious for the gold dimer, for which the quadrupole energy is comparatively large. The different relative importance of the quadrupole component can be understood if one looks at the atomic valence eigenvalues listed in Table IV. In the bismuth atom the $5d$ orbitals are energetically clearly separated from the more weakly bound $6s$ and $6p$ orbitals, so that the $5d$ orbitals do not really participate in the binding: the density of the closed $5d$ subshell also remains essentially spherical (with respect to the nucleus) in the molecule. Thus, its contribution to the Hartree potential is well described by the monopole term $L_H=0$. Thus, while $L_H=1$ is required for the Hartree potential of the $6p$ -orbitals, the quadrupole contribution in the Hartree potential is negligible. In the same way, one can argue for silver that the $4d$ orbitals do not significantly contribute to the binding, so that here again the quadrupole term in the Hartree potential is much less important than the dipole term. In contrast to these two molecules, the $5d$ and $6s$ valence orbitals in the gold atom exhibit near degeneracy and the $5d$ electrons are relevant for the molecular bond, introducing a quadrupole pattern in the molecular valence density. Consequently, the quadrupole contribution in the Hartree potential is sizable (≈ 0.2 eV). However, extending this argument to higher orders, the multipole $L_H=3$ should not give any further correction as the $4f$ -subshell remains spherical in Au_2 —this is supported by the fact that inclusion of additional f functions in the orbital basis does not affect the results (see Sec. III).

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