PHYSICAL REVIEW A VOLUME 59, NUMBER 6 JUNE 1999

Systematic study of the Ib diatomic molecules Cu_2, Ag_2, and Au_2 using advanced relativistic density functionals

S. Varga, E. Engel,* W.-D. Sepp, and B. Fricke
Fachbereich Physik, Universität Kassel, D-34109 Kassel, Germany

(Received 11 January 1999)

In this paper we present results of four-component relativistic density-functional calculations for diatomic molecules with heavy constituents. The fully relativistic treatment of the electron kinematics is used for a consistent examination of the importance of gradient and relativistic corrections to the exchange-correlation energy functional. In agreement with recent scalar relativistic calculations, we find that relativistic corrections to exchange-correlation functionals give no significant contribution to the binding properties of the investigated diatomic molecules. On the other hand, the effect of gradient terms is sizable, leading to a clear improvement of dissociation energies over the standard local-density approximation. The usefulness of gradient contributions in the high-Z regime is nevertheless somewhat questioned by the fact that they overcorrect the small errors in bond lengths found with the local-density approximation. [S1050-2947(99)04506-0]

PACS number(s): 31.15.Ew, 31.15.Ar, 31.30.Jv

I. INTRODUCTION

Density-functional theory (DFT) is a powerful tool for the discussion of ground-state properties of atomic and molecular systems [1,2]. The quality of DFT results depends on the actually applied form of the exchange-correlation (xc) energy functional $E_{xc}[n]$ which provides an effective single-particle description of the xc effects. In general, semilocal xc functionals based on the gradient expansion, the so-called generalized gradient approximations (GGAs), significantly improve results over the standard local-density approximation (LDA). In the nonrelativistic regime both the superior performance of the GGA and the competitiveness of DFT methods with conventional *ab initio* many-body approaches have been impressively demonstrated in [2].

On the other hand, when one deals with atomic and molecular systems in which very heavy elements are involved, a relativistic description is required. This may be achieved either via a fully relativistic four-component formalism or, within a weakly relativistic approximation, via a two- or one-component description based on the decoupling of the large and small spinor components. However, relativistic corrections not only arise in the context of the kinetic energy functional $T_s[n]$, but, in principle, also affect the form of the xc-energy functional. Note that the relativistic correction to the xc energy consists of two contributions: On the one hand, insertion of a self-consistent relativistic density into $E_{xc}[n]$ gives a different result than insertion of a self-consistent nonrelativistic density. This effect, which arises from the relativistic treatment of T_s, is also present for nonrelativistic representations of $E_{xc}[n]$. The second contribution, which is examined here, results from the modification of the functional form of $E_{xc}[n]$ due to the relativistic kinematics of the electrons and the (retarded) Breit contribution to the electron-electron interaction.

The relativistic form of the LDA (RLDA) for exchange has been known for a long time [3,4] and the dominant correction for the LDA correlation is also available [5,6]. However, for atoms it was demonstrated [7,6] that the RLDA by far overestimates the relativistic corrections to the xc energy, in particular for the transverse (retarded Breit) exchange. As a consequence, recently also the GGA concept has been extended to the relativistic domain [8], providing explicit relativistic forms (RGGAs) for the most widely used GGAs by Becke [9] and Perdew [10]. By comparison with exact exchange-only results [11,6] as well as second-order Møller-Plesset data, it was shown [8] that these RGGAs give much more realistic xc energies and xc potentials for high-Z atoms.

However, the relativistic corrections to the functional form of $E_{xc}[n]$ are directly relevant only in the high-density regime, i.e., for the innermost (core) orbitals. Thus the question arises to what extent these contributions actually affect molecular properties. A first study of the impact of relativistic corrections to E_{xc} on the band structures of Pt and Au exhibited small but nevertheless non-negligible effects [12]. However, while in these calculations T_s was treated fully relativistically, the RLDA was used for E_{xc} which may have led to an overestimation. More recently, both the RLDA and the RGGA were applied to diatomic molecules [13]. It was found that the relativistic contributions in the xc functional have only a marginal impact on the binding properties of small molecules. However, these calculations were based on a scalar relativistic form of T_s (neglecting spin-orbit coupling) and only the exchange part of the RGGA was included. It is the aim of the present contribution to reexamine the findings of [13] within a fully relativistic framework. In addition, we investigate the adequacy of the GGA concept for dealing with very heavy constituents, which has recently been questioned in a study of the cohesive properties of $5d$ transition metals [14].

II. THEORY

Relativistic density-functional theory (RDFT), first introduced by Rajagopal [15,3], may be established in a system-

---

*Present address: Sektion Physik, Universität München, Theresienstrasse 37/IV, D-80333 München, Germany.

atic fashion on the basis of quantum electrodynamics [16,17]. The basic quantity in RDFT is the ground-state four-current density $j^{\nu}(\vec{r})$. While in the most general situation j^{ν} also contains vacuum polarization contributions, these quantum electrodynamical effects are irrelevant for molecular electronic structure calculations, so that here we restrict ourselves to the no-pair limit of RDFT from the very outset. The four current is then represented in terms of N discrete auxiliary single-particle spinors ψ_k,

$$j^{\nu}(\vec{r})=(j^0,\vec{j}), \tag{1}$$

$$j^0(\vec{r})=n(\vec{r})=\sum_{-mc^2<\epsilon_k\leq\epsilon_F}\psi_k^{\dagger}(\vec{r})\psi_k(\vec{r}), \tag{2}$$

$$\vec{j}(\vec{r})=\sum_{-mc^2<\epsilon_k\leq\epsilon_F}\psi_k^{\dagger}(\vec{r})\vec{\alpha}\psi_k(\vec{r}). \tag{3}$$

The no-pair approximation not only eliminates the need for renormalization for the divergent vacuum contributions to j^{ν}, but also for the total energy functional $E[j]$ which is decomposed as

$$E[j]=T_s[j]+E_{\rm ext}[j]+E_{\rm H}[j]+E_{\rm xc}[j]. \tag{4}$$

Here T_s represents the kinetic energy of the auxiliary ''particles,''

$$T_s=\sum_{-mc^2<\epsilon_k\leq\epsilon_F}\int d^3r\,\psi_k^{\dagger}(\vec{r})\times[-ic\vec{\alpha}\cdot\vec{\nabla}+(\beta-1)mc^2]\psi_k(\vec{r}), \tag{5}$$

$E_{\rm ext}$ the external potential energy,

$$E_{\rm ext}=\int d^3r\,j^0(\vec{r})v_{\rm ext}(\vec{r}), \tag{6}$$

$E_{\rm H}$ is the direct electronic Hartree energy,

$$E_{\rm H}=\frac{e^2}{2}\int d\vec{r}\int d\vec{r}'\frac{j^{\nu}(\vec{r})j_{\nu}(\vec{r}')}{|\vec{r}-\vec{r}'|}, \tag{7}$$

and $E_{\rm xc}$ denotes the exchange-correlation energy. $E_{\rm H}$ as well as $E_{\rm xc}$ consist of longitudinal (Coulomb) and transverse (retarded Breit) components. However, for closed-shell systems (as the diatomic molecules considered here) the spatial components of j^{ν} and thus the transverse contribution to $E_{\rm H}$ vanish due to time-reversal symmetry. In addition, the transverse Hartree energy is very small for neutral open-shell atoms (for atomic Au it amounts to -0.25×10^{-6} hartrees). We will thus neglect this energy in the following. Note that $\vec{j}=\vec{0}$ does not imply that the transverse xc energy also vanishes (for atomic Hg the transverse exchange energy is as large as 22 hartrees).

All relativistic xc functionals developed so far are functionals of the density n only. This is immediately clear for the RLDA, as $\vec{j}$ vanishes for the relativistic homogeneous electron gas (HEG), which is the basis for the RLDA. But also the relativistic forms of the GGA have been constructed as functionals of n only [8], which is legitimate in view of the fact that, for systems not subject to external magnetic fields, $\vec{j}$ can be understood as a functional of n [6,17]. As a consequence, the complete $E[j]$ reduces to a functional of only the density, $E[n]$. Minimization of $E[n]$ with respect to the auxiliary orbitals ψ_k leads to the relativistic Kohn-Sham equations (RKS),

$$\{[-ic\vec{\alpha}\cdot\vec{\nabla}+(\beta-1)mc^2]+v_{\rm ext}(\vec{r})+v_{\rm H}(\vec{r})+v_{\rm xc}(\vec{r})\}\psi_k=\epsilon_k\psi_k, \tag{8}$$

where $v_{\rm ext}$ represents the interaction of the electrons with the nuclear charges Z_{α},

$$v_{\rm ext}(\vec{r})=-\sum_{\alpha}\int\frac{Z_{\alpha}e^2n(\vec{r})}{|\vec{R}_{\alpha}-\vec{r}|}d^3r, \tag{9}$$

and $v_{\rm H}$ is the electronic Coulomb (Hartree) potential,

$$v_{\rm H}(\vec{r})=e^2\int\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'. \tag{10}$$

Finally, $v_{\rm xc}$ is the xc potential, which is defined as the functional derivative of the xc energy functional with respect to n,

$$v_{\rm xc}(\vec{r})=\frac{\delta E_{\rm xc}[n]}{\delta n(\vec{r})}. \tag{11}$$

For $E_{\rm xc}[n]$ we have examined several combinations. For the nonrelativistic LDA the standard exchange is combined with the Vosko-Wilk-Nusair (VWN) [18] parametrization for correlation. Accordingly, the RLDA for the exchange energy [3,4] is used with a relativistic version of the VWN functional [14], in which the relativistic corrections are taken into account on the level of the random-phase approximation (RPA),

$$E_{\rm xc}^{\rm RLDA}[n]=\int d^3r[e_x^{\rm HEG}(n)\Phi_{x,0}(\beta)+e_c^{\rm VWN}(n)\Phi_{c,0}^{\rm RPA}(\beta)], \tag{12}$$

where

$$e_x^{\rm HEG}(n)=-\frac{3(3\pi^2)^{1/3}e^2}{4\pi}n^{4/3};\qquad \beta=\frac{(3\pi^2n)^{1/3}}{mc}, \tag{13}$$

and the relativistic correction factors Φ are given by

$$\Phi_{x,0}(\beta)=1-\frac{3}{2}\left[\frac{\sqrt{1+\beta^2}}{\beta}-\frac{\operatorname{arcsinh}(\beta)}{\beta^2}\right], \tag{14}$$

$$\Phi_{c,0}^{\rm RPA}(\beta)=\frac{1+a_1\beta^3\ln(\beta)+a_2\beta^4+a_3(1+\beta^2)^2\beta^4}{1+b_1\beta^3\ln(\beta)+b_2\beta^4+b_3[A\ln(\beta)+B]\beta^7} \tag{15}$$

[for the coefficients a_i, b_i see Table I; $A=(1-\ln 2)/\pi^2$ and $B=-0.2037$ are known from the nonrelativistic high-density limit]. For the gradient corrected exchange functionals we

TABLE I. Parameter sets for the relativistic correction factors (15, 17, 18) of the RLDA and RPW91-GGA (the corresponding values for RB88 are essentially identical—compare [8]).

	Exchange		Correlation	
	$\Phi^L_{x,2}$	$\Phi^T_{x,2}$	$\Phi^{\rm RPA}_{c,0}$	$\Phi^{\rm GGA}_{c}$
Parameter	PW91	PW91	LDA	PW91
a_1	2.2156	3.5122	-2.44968	1.9407
a_2	0.66967	0.62525	1.91853	0.14435
a_3			0.0718854	
b_1	1.3267	1.3313	-1.59583	0.28142
b_2	0.79420	0.10066	1.29176	0.004723
b_3			0.364044	

have used both the Becke (B88) [9] and the Perdew-Wang (PW91) [10] form as well as their relativistic extensions (RPW91,RB88) [8],

$$E_x^{\rm RGGA}=\int d^3r\, e_x^{\rm HEG}(n)[\Phi_{x,0}(\beta)+g_x^{\rm GGA}(n,(\vec{\nabla}n)^2)\Phi_{x,2}(\beta)]. \tag{16}$$

The relativistic correction factor $\Phi_{x,2}$ contains both a longitudinal and a transverse component, $\Phi_{x,2}=\Phi^L_{x,2}+\Phi^T_{x,2}$,

$$\Phi^L_{x,2}=\frac{1+a_1^L\beta^2+a_2^L\beta^4}{1+b_1^L\beta^2+b_2^L\beta^4},\quad \Phi^T_{x,2}=\frac{a_1^T\beta^2+a_2^T\beta^4}{1+b_1^T\beta^2+b_2^T\beta^4} \tag{17}$$

(parameters in Table I). The (R)B88 GGA has been augmented by the 86 version of Perdew's GGA for correlation [19], while in the case of (R)PW91 the appropriate PW91-GGA for correlation [10] is added. In the latter case also the relevance of relativistic corrections to the correlation functional is investigated, utilizing a semiempirical relativistic extension of the PW91-GGA [8],

$$E_c^{\rm RGGA}[n]=\int d^3r\, e_c^{\rm GGA}(n,(\vec{\nabla}n)^2)\Phi_c^{\rm GGA}(\beta), \tag{18}$$

with $\Phi_c^{\rm GGA}$ being of the same form as $\Phi^L_{x,2}$.

III. COMPUTATIONAL DETAILS

In our linear combination of atomic orbitals (LCAO) approach the molecular RKS spinors ψ_k are expanded in numerical, atom-centered, Dirac spinors ξ_μ,

$$\psi_k(\vec{r})=\sum_{\mu n\kappa m} c_k^{\mu n\kappa m}\xi_\mu^{n\kappa m}(\vec{r}),$$

$$\xi_\mu^{n\kappa m}(\vec{r})=\frac{1}{r}\begin{pmatrix} f_\mu^{n\kappa}(r)\mathcal{Y}_\kappa^m(\Omega)\\ ig_\mu^{n\kappa}(r)\mathcal{Y}_{-\kappa}^m(\Omega)\end{pmatrix} \tag{19}$$

with f,g being the radial parts of the large and small spinor components and μ denoting the μth orbital with main quantum number n and magnetic quantum number m (i.e., μ goes through all centers in the molecule of interest). κ is the standard angular momentum quantum number

$$\kappa=\begin{cases}-(j+1/2)=-(l+1) & \text{for}\quad j=l+1/2\\ j+1/2=l & \text{for}\quad j=l-1/2.\end{cases} \tag{20}$$

The RKS equations (8) can then be recast as an algebraic eigenvalue problem,

$$\mathbf{Hc}=\epsilon\mathbf{Sc}, \tag{21}$$

with the matrix elements of the RKS single-particle Hamiltonian in Eq. (8) abbreviated by **H** and the overlap matrix by **S**.

All matrix elements in Eq. (21) are evaluated with the numerical multicenter integration scheme by Baerends [20]. To reduce the singularities of the relativistic orbitals originating from the nuclear potential at the origin, mesh points and weights are shifted towards smaller r values. This leads to an accuracy of 10^{-7} even for the most critical matrix elements.

The most time-consuming step in the self-consistent solution of Eq. (21) is the calculation of the Hartree potential and energy. For our numerically given basis functions, direct use of Eqs. (10) and (7) with the density (2) would require two subsequent three-dimensional integrations on the full integration grid. To simplify these integrations we use a special variationally consistent density fit procedure [21]. Decomposing the electronic density into a dominant contribution $\tilde{n}$, whose components f_α are spherical with respect to one of the atomic centers in the molecule, and a remainder $\triangle n$,

$$n(\vec{r})=\tilde{n}(\vec{r})+\triangle n(\vec{r});\quad \tilde{n}(\vec{r})=\sum_\alpha f_\alpha(|\vec{r}-\vec{R}_\alpha|), \tag{22}$$

with

$$\int d^3r\,\tilde{n}(\vec{r})=\int d^3r\, n(\vec{r})=N,$$

leads to a corresponding decomposition of $v_{\rm H}$ and $E_{\rm H}$,

$$v_{\rm H}(\vec{r})=\tilde{v}_{\rm H}(\vec{r})+e^2\int\frac{\triangle n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r';$$

$$\tilde{v}_{\rm H}(\vec{r})=e^2\int\frac{\tilde{n}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r', \tag{23}$$

$$E_{\rm H}=\tilde{E}_{\rm H}+\triangle E_{\rm H}, \tag{24}$$

$$\tilde{E}_{\rm H}=\int\tilde{v}_{\rm H}(\vec{r})n(\vec{r})d\vec{r}-\frac{e^2}{2}\int\int\frac{\tilde{n}(\vec{r})\tilde{n}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r', \tag{25}$$

$$\triangle E_{\rm H}=\frac{e^2}{2}\int\int\frac{\triangle n(\vec{r})\triangle n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r\,d^3r'. \tag{26}$$

Both $\tilde{v}_{\rm H}$ and $\tilde{E}_{\rm H}$ are easily evaluated, so that we neglect $v_{\rm H}-\tilde{v}_{\rm H}$ and $\triangle E_{\rm H}$ in our calculations in order to enhance the computational efficiency. The form of $\tilde{n}$, i.e., of the f_α, is determined by minimizing $\triangle E_{\rm H}$ and thus the error induced

TABLE II. Optimized atomic basis sets for the diatomic molecular calculations. ID is the degree of ionization.

	n	Minimal basis	ID of np orbitals	ID of nd orbitals
Cu	4	s	1.5	4.0
Ag	5	s	1.5	4.0
Au	6	s	2.0	5.5

by neglect of $v_{\rm H}-\tilde{v}_{\rm H}$ and $\triangle E_{\rm H}$. The details of this modified numerical integration scheme and the density fit procedure may be found in [22].

In all molecular calculations we use energy-adjusted basis functions. In a first step we calculate the Born-Oppenheimer energy surface with a minimal basis set in order to determine the energy minimum. This minimal basis set consists of just the valence ns orbitals ($n=4,5,6$ for Cu, Ag, Au), i.e., of the orbitals present in the atomic ground state. At the resulting energy minimum we add p orbitals of slightly ionized atoms. In view of the exponentially decaying $v_{\rm xc}$ of both the LDA and the GGA, the ionization is required for obtaining bound unoccupied valence states. The degree of ionization is subsequently varied to determine that value which minimizes the molecular energy. Increasing (decreasing) the degree of ionization shifts the maxima of the p orbitals inward (outward), so that in this procedure these maxima are moved to the bonding region. This procedure is repeated for d orbitals. The final optimized basis sets are listed in Table II for the three elements Cu, Ag, and Au.

To evaluate the binding energy one has to subtract the total energies of the atoms from the molecular values. In contrast to the molecular calculations, the minimal basis is appropriate for the calculation of the atomic reference energies. All atomic data were also obtained with our molecular code, i.e., on the same numerical grid. In doing so we hope to cancel numerical errors as much as possible. However, it is important to note that this implies the use of the LDA/GGA, rather than the corresponding spin-density functionals, for the atomic ground states with their unpaired s electrons.

Finally, we remark that the gradient corrections have been treated in a perturbative fashion, the reason being the fact that a self-consistent solution of the RKS equations (8) in the case of the (R)GGA requires the second derivatives of the density. The highly accurate evaluation of the second derivatives within our calculational scheme (using numerical basis functions) is rather time-consuming. On the other hand, the xc energy only depends on the density and its first gradient, which is much easier to evaluate and much more stable. We have thus solved the RKS equations (21) on the (R)LDA level. Subsequently, we have inserted the RLDA density and its gradient into the GGA functionals to calculate the total energy. This procedure has been applied by various authors in the nonrelativistic case [1,23]. Comparison to fully self-consistent results (where these are available) demonstrates its adequacy (see, e.g., [9,1] and Sec. IV B). For all calculations we have used point nuclei and $c=137.036$ a.u.

IV. RESULTS

A. Atomic results

Before concentrating on the molecular calculations, we first check the accuracy of our numerical method in the atomic situation. For this purpose we compare our results with data obtained with a fully numerical, finite difference code for closed-subshell (spherical) atoms [6]. Evaluated on radial grids of 800 mesh points, the finite difference results can serve as exact reference numbers. A detailed analysis shows that the data from the two codes are very close. For the gold atom, the eigenvalues of all relevant orbitals ($1s_{1/2}$-$6s_{1/2}$) differ by less than 0.04 mhartrees (on the LDA level).

Table III shows some energy components (evaluated perturbatively in the case of the GGA). While the total energies differ by less than 0.1 mhartrees in the case of the RLDA, we find a deviation of less than 0.2 mhartree for the RGGA, even for the heaviest atom, gold. Most of this error is presumably accumulated in the core region, so that we expect the numerical errors in our energy surfaces to be clearly below 0.01 eV. Note, however, that the systematic error introduced by neglecting $v_{\rm H}-\tilde{v}_{\rm H}$ and $\triangle E_{\rm H}$ does not show up for the spherical atomic densities considered here.

B. Molecular results

In Tables IV–VI we present the spectroscopic constants which we have obtained for Cu_2, Ag_2, and Au_2 with various xc functionals. For comparison, the results of two scalar-relativistic calculations are also listed. Van Lenthe *et al.* [24] have used a scaled (gauge invariant) zeroth-order regular ap-

TABLE III. xc-energy components and total energy of copper, silver, and gold: Comparison of data obtained with the molecular code (MC) with highly accurate atomic reference results (AC) (the RGGA values have been calculated by insertion of RLDA densities into the RGGA). RGGA refers to the x/c combination RB88/P86 (all energies in hartrees).

		$-E_x$		$-E_c$		$-E_{\rm tot}$	
		RLDA	RGGA	RLDA	RGGA	RLDA	RGGA
Cu	AC	60.93336	65.67777	2.57508	1.52864	1650.92180	1654.61978
	MC	60.93334	65.67776	2.57508	1.52864	1650.92179	1654.61977
Ag	AC	132.97413	143.21019	4.52446	2.81339	5305.53427	5314.05926
	MC	132.97412	143.21017	4.52446	2.81336	5305.53425	5314.05921
Au	AC	307.09099	335.73223	8.50599	5.48120	18998.83460	19024.45105
	MC	307.09099	335.73233	8.50599	5.48105	18998.83449	19024.45089

TABLE IV. Bond length, bond distance, and frequency from various molecular calculations for Cu_2: Present work (pw) in comparison to scalar relativistic results and experimental data.

	Functional		R_e	D_e (up)	D_e (sp)	ω	
t	x	c	(Bohr)	(eV)	(eV)	(cm^{-1})	Ref.
R	RLDA	RLDA	4.09	3.65	(3.24)	301	pw
SR	RLDA	RLDA	4.05		2.85	306	[13]
SR	RLDA	RLDA	4.06		2.77	298	[24]
R	RB88	RLDA	4.29	2.72		265	pw
R	B88	LDA	4.29	2.72		265	pw
R	RB88	P86	4.20	3.21	(2.73)	283	pw
R	RPW91	RPW91	4.21	3.27		282	pw
R	PW91	PW91	4.20	3.27		283	pw
SR	B88	P86	4.16		2.27	285	[13]
SR	B88	P86	4.18		2.19	272	[24]
	Expt.		4.20	2.05		265	[27]

proximation (ZORA) one-electron Hamiltonian. In this work the gradient corrections have been added perturbatively as in our calculations. In contrast, Mayer *et al.* [13] have included the gradient terms self-consistently, using a second-order Douglas-Kroll scheme for T_s. Both methods neglect spin-orbit coupling explicitly, while spin-orbit coupling is inherently included in our four-component approach.

Each of the tables is structured in the following way: In the first row (t) the treatment of the kinetic energy T_s is characterized, with R denoting fully relativistic and SR denoting scalar-relativistic calculations. The columns labeled with x and c indicate which exchange and correlation functionals are used. The bond distances R_e, dissociation energies D_e, and vibrational frequencies ω have been obtained by fitting the numerical energy surface to a Morse potential. In the case of D_e, two types of data are distinguished: While for the scalar-relativistic calculations without spin-orbit coupling the spin-dependent (sp) versions of the LDA and GGA have been utilized [25], our fully relativistic approach is based on the unpolarized (up) forms of these functionals. Although this conceptual difference does not affect the ground-state energies of the dimers considered here, it leads to significant shifts in the corresponding atomic ground-state energies, and thus in D_e. Its size can be estimated from strictly nonrelativistic DFT calculations, combining a spin-dependent treatment of T_s with either the sp or the up versions of the LDA/GGA. For instance, for Cu the sp ground-state energy is 0.20 eV lower than the up energy in the case of the LDA. This difference increases to 0.24 eV for the B88/P86-GGA. Adding these corrections to the up dissociation energies yields the numbers in parentheses (this procedure is often used to correct for spin-polarized atomic ground states — see, e.g., [26]). Note that the bond lengths and zero point energies are not affected by this conceptual problem, so that the R_e and ω values allow for a more serious comparison between the different calculations.

TABLE V. As Table IV for Ag_2.

	Functional		R_e	D_e (up)	D_e (sp)	ω	
t	x	c	(Bohr)	(eV)	(eV)	(cm^{-1})	Ref.
R	RLDA	RLDA	4.78	2.84	(2.51)	207	pw
SR	RLDA	RLDA	4.73		2.25	209	[13]
SR	RLDA	RLDA	4.69		2.28	208	[24]
R	RB88	RLDA	5.02	1.96		175	pw
R	B88	LDA	5.02	1.96		175	pw
R	RB88	P86	4.91	2.39	(1.99)	191	pw
R	RPW91	RPW91	4.91	2.45		193	pw
R	PW91	PW91	4.90	2.45		193	pw
SR	B88	P86	4.87		1.67	185	[13]
SR	B88	P86	4.84		1.71	183	[24]
	Expt.		4.78	1.66		192	[27]

TABLE VI. As Table IV for Au_2.

	Functional		R_e	D_e (up)	D_e (sp)	ω	
t	x	c	(Bohr)	(eV)	(eV)	(cm^{-1})	Ref.
R	RLDA	RLDA	4.69	3.65	(3.34)	201	pw
SR	RLDA	RLDA	4.65		2.92	191	[13]
SR	RLDA	RLDA	4.64		2.92	193	[24]
R	RB88	RLDA	4.89	2.59		172	pw
R	B88	LDA	4.88	2.60		172	pw
R	RB88	P86	4.79	3.11	(2.74)	187	pw
R	RPW91	RPW91	4.79	3.17		187	pw
R	PW91	PW91	4.78	3.19		188	pw
SR	B88	P86	4.76		2.27	177	[13]
SR	B88	P86	4.75		2.26	174	[24]
	Expt.		4.67	2.30		191	[27]

First of all, we examine the relevance of the relativistic corrections to the xc functionals for molecular data. The x/c combinations B88/LDA and PW91/PW91 have been applied both in their nonrelativistic and their relativistic forms. Looking at the resulting spectroscopic constants, all three dimers confirm the conclusion of Mayer *et al.* [13] that relativistic corrections to $E_{\mathrm{xc}}[n]$ are irrelevant for molecular properties, their maximum impact being a shift of 0.01 Bohr in R_e. We will thus identify the relativistic and nonrelativistic forms of all xc functionals in the following.

Next, we compare the scalar and fully relativistic results. For each dimer both the RLDA and the B88/P86-GGA have been used by van Lenthe *et al.* [24], Mayer *et al.* [13], and in the present study. Van Lenthe *et al.* and Mayer *et al.* essentially agree for all spectroscopic parameters (within 0.04 Bohr for R_e and 0.08 eV for D_e), which emphasizes the equivalence of the perturbative and the self-consistent treatment of the gradient terms. Our bond lengths, on the other hand, are 0.03–0.07 Bohr larger. This trend is somewhat more pronounced for Ag_2 than for Au_2, so that it must be attributed to our approximate treatment of $E_{\mathrm{H}}[n]$, rather than to the different handling of spin-orbit coupling. As explained earlier, a comparison of the corresponding dissociation energies is not straightforward. Nevertheless, including the spin contributions to atomic ground-state energies (obtained in the strictly nonrelativistic limit) in a perturbative manner, one finds that our binding energies are more attractive than the results of [24] and [13]: For Cu_2 and Au_2 our D_e's are roughly 0.45 eV larger, for Ag_2 0.3 eV. For all three dimers these differences are essentially independent of the xc functional used, which is a clear hint that the combined neglect of

$v_{\mathrm{H}}-\widetilde{v}_{\mathrm{H}}$ and $\triangle E_{\mathrm{H}}$ is responsible for these shifts in D_e (while a minor contribution to the shifts could originate from the different treatment of the spin and relativity).

Finally, we analyze the importance of gradient corrections to the xc energy. By successively adding in gradient corrections for exchange and correlation one finds that the exchange GGA expands the bonds by roughly 0.2 Bohr, while the correlation GGA reduces R_e by about 0.1 Bohr. Accompanying effects are observed in D_e and ω. As the mixed combination B88/LDA always clearly overestimates R_e, consistent inclusion of gradient corrections for both the x and the c part of the xc functional seems mandatory.

In order to investigate the properties of gradient corrections in the high-Z regime, we thus focus on the x/c combinations B88/P86 and PW91/PW91. It is well known that, in general, the LDA underestimates bond lengths (and correspondingly overestimates atomization energies and vibrational frequencies) and that the GGA tends to correct these errors. Our results for Cu_2 are consistent with this general statement: With the LDA, R_e is found to be roughly 0.1 Bohr too small and D_e is about 1.2 eV too large (on the basis of the sp values). Using the GGAs these errors are reduced by about a factor of 2. However, for Ag_2 and, in particular, for Au_2 the LDA gives bond lengths in rather good agreement with experiment. Thus, while the GGA clearly improves this quantity over the LDA for Cu_2, it overcorrects the LDA's errors for Ag_2 and Au_2 (leading to deviations of 2–3 % from the experimental R_e). This neither depends on the specific form of the GGA used (B88/P86 and PW91/PW91 give very similar results for all molecules considered here), nor is it due to our handling of $E_{\mathrm{H}}[n]$ (the same observation can be made for the scalar-relativistic results). In fact, this finding is in perfect agreement with the results of a recent study of metallic gold and platinum [14]. On the other hand, the D_e's obtained with the GGAs for Ag_2 and Au_2 are definitively closer to the experimental values than the LDA energies.

V. CONCLUSION

The results for the Ib diatomic molecules Cu_2, Ag_2, and Au_2 summarized in Tables IV–VI clearly show the quality of relativistic DFT results available at present. In spite of the remaining errors, these results demonstrate the predictive power of relativistic DFT calculations in the high-Z regime. In fact, the highly relativistic system Au_2 is as well described as the weakly relativistic system Cu_2. The relativistic DFT approach thus seems particularly adequate for the description of more complex molecular systems with very heavy constituents.

As far as the importance of relativistic corrections to the xc-energy functional is concerned, our results support the conclusion of Mayer *et al.* [13]: While these corrections are sizable in the individual total energies of molecules and atoms, their contributions cancel out in dissociation energies. At least on the present level of sophistication, relativistic corrections to the xc-energy functional can be safely neglected in molecular calculations.

Finally, our results indicate that for molecules with very heavy constituents the GGA concept is not quite as successful as for molecules with light constituents: While the energetics of all dimers considered here are improved by the GGA as compared with the LDA, the GGA overcorrects the rather small errors of the LDA in the bond geometries (and thus the vibrational frequencies) for Ag_2 and, in particular, for Au_2. Although this aspect requires further confirmation by a large scale study of heavy molecules (including also *p* and *d* binding, where the spin-orbit splitting directly plays a role), it presently seems that in the high-Z regime the LDA gives more realistic bond lengths than the GGA.

ACKNOWLEDGMENTS

We would like to thank E. van Lenthe for helpful correspondence. S.V. acknowledges financial support by the Deutsche Forschungsgemeinschaft (DFG) under Project No. Fr 637/8-1,2.

---

[1] A. D. Becke, J. Chem. Phys. **96**, 2155 (1992).
[2] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **98**, 5612 (1993).
[3] A. K. Rajagopal, J. Phys. C **11**, L943 (1978).
[4] A. H. MacDonald and S. H. Vosko, J. Phys. C **12**, 2977 (1979).
[5] M. V. Ramana and A. K. Rajagopal, Phys. Rev. A **24**, 1689 (1981).
[6] E. Engel, S. Keller, A. Facco Bonetti, H. Müller, and R. M. Dreizler, Phys. Rev. A **52**, 2750 (1995).
[7] M. V. Ramana, A. K. Rajagopal, and W. R. Johnson, Phys. Rev. A **25**, 96 (1982).
[8] E. Engel, S. Keller, and R. M. Dreizler, Phys. Rev. A **53**, 1367 (1996); in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by by J. F. Dobson, G. Vignale, and M. P. Das (Plenum, New York, 1998), p. 149.
[9] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[10] J. P. Perdew, in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), p. 11.
[11] E. Engel, A. Facco Bonetti, S. Keller, I. Andrejkovics, and R. M. Dreizler, Phys. Rev. A **58**, 964 (1998).
[12] A. H. MacDonald, J. M. Daams, S. H. Vosko, and D. D. Koelling, Phys. Rev. B **23**, 6377 (1981); **25**, 713 (1982).
[13] M. Mayer, O. D. Häberlen, and N. Rösch, Phys. Rev. A **54**, 4775 (1996).
[14] R. N. Schmid, E. Engel, R. M. Dreizler, P. Blaha, and K. Schwarz, Adv. Quantum Chem. **33**, 209 (1999).
[15] A. K. Rajagopal and J. Callaway, Phys. Rev. B **10**, 1 (1973).
[16] A. K. Rajagopal, Phys. Rev. A **50**, 3759 (1994).
[17] E. Engel and R. M. Dreizler, in *Density Functional Theory II*, edited by R. F. Nalewajski, Topics in Current Chemistry Vol. 181 (Springer, Berlin, 1996), p. 1.
[18] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[19] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986); **34**, 7406(E) (1986).

[20] P. M. Boerritger, G. TeVelde, and E. J. Baerends, Int. J. Quantum Chem. **33**, 87 (1988).

[21] B. I. Dunlap, J. W. D. Conolly, and J. R. Sabin, J. Chem. Phys. **71**, 4993 (1979).

[22] T. Baştuğ, D. Heinemann, W.-D. Sepp, D. Kolb, and B. Fricke, Chem. Phys. Lett. **211**, 119 (1993).

[23] L. Fan and T. Ziegler, J. Chem. Phys. **95**, 7401 (1991).

[24] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 1272 (1994).

[25] E. van Lenthe (private communication).

[26] M. Fuchs, M. Bockstedte, E. Pehlke, and M. Scheffler, Phys. Rev. B **57**, 2134 (1998).

[27] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure I* (Van Nostrand Reinhold, New York, 1950).