Relativistic Density Functional Calculations for Pt_2

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First full-relativistic density functional calculations with the extension of the spin-polarization functional for the relativistic density functional theory in their collinear and noncollinear form are presented here for the molecular system Pt_2. The agreement with experiment is very good.

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Introduction.—In the last two decades many spectroscopic studies of diatomic transition metals of the 3*d* and 4*d* periods have been published (see [1] and references therein). Through this work the basic electronic structure of the homometallic and heterometallic 3*d* and 4*d* dimers has been discerned and a qualitative understanding of many of these molecules has been established. In contrast, the present knowledge of the 5*d* transition metal dimers is much more limited. For instance, Pt_2 is the only element with an open 5*d* subshell for which the bond length has been measured.

A new experimental investigation of Pt_2 has recently been published [1]. Airola and Morse were able to measure for the first time the resolved rotational spectrum of the Pt_2 molecule. They determined very precise values for the bond energy, bond length, and the ground-state vibrational frequency. Using different isotopes it was also possible to determine the ground-state symmetry of the electronic system. They compared the ground-state properties with that of the Au_2 molecule and pointed out the big influence of the open 5*d* shell of Pt on the bond energy and the bond length. They also emphasized that there was no theoretical *ab initio* method at that time which could properly include relativistic effects and electron correlation. Although in a rigorous sense this still is true we present here a density functional calculation which comes very close to this goal.

The first complete theoretical study of Pt_2 using a complete active space self-consistent field first-order configuration interaction method has been done by Balasubramanian [2]. While the ground-state symmetry obtained in [2] is in agreement with the experimental findings the bond length is slightly too long and the vibrational frequency too low. The calculated bond energy represents only 63% of the measured value. More recent calculations by Wang and Carter [3] using a similar method lead to an even worse result for the bond energy (see also Table I).

An alternative approach is the density functional theory (DFT). DFT calculations depend on the choice of the exchange-correlation functional and the treatment of the kinetic energy. The spectrum of the different approximations of the kinetic energy starts with a purely nonrelativistic approach with or without spin-orbit interaction, continues with the zeroth-order regular approximation (ZORA) [11,12] and ends with a full-relativistic description. A comparison of these approximations and corresponding results can be found in [9,13]. In this paper we use the best possible method, i.e., the full-relativistic treatment, for the kinetic energy. Because of this all direct and indirect relativistic effects are included in our calculations.

In the last three decades a series of different approximations for the exchange and correlation functionals were introduced. An overview can be found in [14]. All these functionals can be written in either relativistic or nonrelativistic form [4]. The two forms lead to different total energies, but almost the same bond energies and bond lengths in the case of molecules [13]. Therefore we will not distinguish between these two forms and the results for one form represent also the results for the other one.

A further difference between various density functionals is the treatment of the spin of the electrons. In the simplest form of nonrelativistic density functionals spin is completely neglected. This approximation works quite well for closed shell systems but leads to wrong results for open shell molecular as well as atomic systems. A very important improvement was achieved by extending these functionals to spin-polarized (SP) forms [15]. In a relativistic description the spin should actually be included in the relativistic form of the density functionals, which depend on the four current density directly, but this approach is not yet suitable for practical applications. Alternatively, the spin can be included into the relativistic form of the density functionals in a theoretical consistent way via the magnetization density using a fictitious external magnetic field which is set to zero in the end formulas (see for more details [14]). In this case the exchange and/or correlation functionals depend not only on the density but also on the magnetization density (see details in [14,16]). The magnetization density at any point in space is defined as magnetic moment per volume [17].

TABLE I. Ground state properties of Pt_2. The abbreviation RLDA means the relativistic local density approximation for exchange only [4], PW91 means both the exchange and correlation functionals from Perdew and Wang [5], B88 means the exchange only functional from Becke [6], P86 means the correlation functional from Perdew [7], and VWN means the correlation functional from Vosko *et al.* [8].

Reference	Method	D_e (eV)	R_e (a.u.)	$\omega(\mathrm{cm}^{-1})$
This work	X_α (0.7)	4.85	4.36	240
This work	X_α (0.7) (SP)	3.69	4.36	235
This work	X_α (0.7) (SP,non)	3.22	4.36	230
This work	RLDA/VWN	4.97	4.35	243
This work	RLDA/VWN (SP)	4.19	4.35	239
This work	RLDA/VWN (SP,non)	4.00	4.35	235
This work	PW91/PW91	4.36	4.42	228
This work	PW91/PW91 (SP)	3.33	4.42	225
This work	PW91/PW91 (SP,non)	3.18	4.42	223
This work	B88/P86	4.28	4.42	228
This work	B88/P86 (SP)	3.28	4.42	225
This work	B88/P86 (SP,non)	3.12	4.42	224
[2]	CASSCF-FOCI	1.97	4.64	189
[3]	CASSCF	1.16	5.18	161
[9]	RGGA	3.94	4.52	234
[10]	LSDA	4.92	4.26	267
[10]	BLYP	3.58	4.38	239
[1]	Expt.	3.14 ± 0.02	4.408 67 (83)	222.46 ± 0.66

Following this, it is a vector which, in general, points to different directions at different points in space. In order to simplify the calculations in most implementations the magnetization density is aligned to the axis of the highest symmetry (z axis), which in the literature is called the collinear approximation. In this approximation the electronic system can have a total magnetic moment even in the case when the real system does not (e.g., closed shell). Generally speaking, this is inconsistent because the exchange-correlation potential in this case is not source free as it should be because it is derived from a vector potential [18]. This is corrected in the so-called noncollinear theory [16,19] where the magnetization density can point to any direction in space. As it is shown in [16] for closed subshell atoms the surfaces of constant magnetization density in the noncollinear case are closed and therefore any total magnetic moment does not appear. In the collinear approximation these plains are perpendicular to the z axis. The difference in the total energy for closed (sub)shells between both descriptions is very small. The authors of Ref. [16] who investigate homologue elements of Pb in the periodic table claim that this should also be valid for open shell atoms. The problem is that these atoms are open shell systems only in a nonrelativistic theory. In a relativistic description, however, these are atoms with a closed subshell. Therefore this result cannot be applied to all open shell systems. We show in this paper that for real open shell systems the difference in the total (bond) energy between the collinear and noncollinear description is about 0.1 eV per atom. Moreover, we will show that DFT in their noncollinear form can reproduce very well the experimental results.

Method.—The complete method will be published elsewhere [20], therefore we give only a brief outline of it in this Letter. Within the density functional method [4,14] the total energy of a molecular system is given by the expression

$$E = \sum_{i=1}^{M} \langle\psi|\, \hat{t}\, |\psi\rangle + \int V^N \rho \, d^3\vec{r} + \frac{1}{2}\int V^H \rho \, d^3\vec{r} + E^{xc}[\rho, \vec{m}] + \sum_{p>q} \frac{Z_p Z_q}{|\vec{R}_p - \vec{R}_q|}, \tag{1}$$

with the density ρ and magnetization density $\vec{m}$ which are defined by

$$\rho(\vec{r}) = \sum_{i=1}^{M} n_i\, \psi_i^+(\vec{r})\psi_i(\vec{r}), \tag{2}$$

$$\vec{m}(\vec{r}) = -\mu_B \sum_{i=1}^{M} n_i \psi_i^+(\vec{r})\beta\vec{\Sigma}\psi_i(\vec{r}). \tag{3}$$

Here n_i are the occupation numbers, $\vec{r}$, $\vec{R}_q$ are the electronic and nuclear coordinates, respectively, and μ_B is the Bohr magneton. The index i runs over all occupied molecular orbitals M, which in our case are four-component Dirac spinors. The four-component spin operator $\vec{\Sigma} = (\Sigma_x, \Sigma_y, \Sigma_z)$ is built from the two-component Pauli matrix

σ. The Dirac kinetic energy operator has the form (we use atomic units throughout)

$$\hat{t} = c\vec{\alpha} \cdot \hat{\vec{p}} + c^2(\beta - I), \tag{4}$$

where $\vec{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are the four-component Dirac matrices in the standard representation [21] and I is the four-component unit matrix.

V^N is the nuclear potential and V^H the electronic Hartree potential. Since the calculation of the Hartree potential from the SCF density (2) is very time consuming, we approximate ρ in (2) by a model density $\tilde{\rho}$. We expand our model density into series of "atomic" multipole densities centered on the nuclei. To determine the expansion coefficients we minimize the difference of Hartree energies calculated from the SCF density ρ and calculated from the model density $\tilde{\rho}$. This procedure leads to small corrections to the total energy (1) which are no longer linear, but quadratic in the difference $\rho - \tilde{\rho}$[22].

E^{xc} is the exchange-correlation energy functional. We use in this work both local functionals, such as Slater X_α and relativistic local-density-approximation (RLDA) as well as nonlocal, gradient corrected functionals from Becke [6], and Perdew [5,7].

The variation of the energy functional (1) leads to the relativistic Kohn-Sham (KS) equations in their noncollinear form for the molecular orbitals ψ_i

$$\left\{\hat{t} + V^N + \tilde{V}^H + \frac{\delta E^{xc}[\rho, \vec{m}]}{\delta \rho} - \mu_B \beta \vec{\Sigma} \cdot \frac{\delta E^{xc}[\rho, \vec{m}]}{\delta \vec{m}}\right\}\psi_i = \epsilon_i \psi_i, \qquad i = 1, \ldots, M'. \tag{5}$$

Here $\tilde{V}^H$ is the Hartree potential from the model density and $M' \geq M$ is the number of molecular orbitals.

If the magnetization density is aligned to the symmetry (z) axis we can use the generalized spin densities [14]

$$\rho_\pm(\vec{r}) = \frac{1}{2}\left[\rho(\vec{r}) \mp \frac{1}{\mu_B} m_z(\vec{r})\right] = \sum_{i=1}^{M} n_i \psi_i^+ \frac{1 \pm \beta \Sigma_z}{2} \psi_i \tag{6}$$

and the KS equations (5) can be written in the form

$$\left\{\hat{t} + V^N(\vec{r}) + \tilde{V}^H(\vec{r}) + \frac{1 + \beta\Sigma_z}{2} V_+^{xc}(\vec{r}) + \frac{1 - \beta\Sigma_z}{2} V_-^{xc}(\vec{r})\right\}\psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}), \tag{7}$$

with

$$\begin{aligned} V_\pm^{xc}(\vec{r}) &= \frac{\delta E^{xc}[\rho_+, \rho_-]}{\delta \rho_\pm} \\ &= \frac{\delta E^{xc}[\rho, m_z]}{\delta \rho} \mp \mu_B \frac{\delta E^{xc}[\rho, m_z]}{\delta m_z}. \end{aligned}$$

A comparison of Eq. (6) with the nonrelativistic definition shows that the spin densities in the relativistic case have a contribution from the large component as well as from the small component. Because of this, an electron cannot be fully spin polarized. This conforms with the well-known statement that the spin is not a "good" quantum number in the relativistic theory.

Results and discussion.—For all calculations of Pt_2 which are presented in Table I we used an optimized basis set. In order to achieve this optimization we started with numerical minimal basis functions for a neutral Pt atom. In the second step we added the additional basis functions $6p1/2$ and $6p3/2$ from a calculation of a Pt atom with a defined degree of ionization. We made several molecular calculations with different partial occupation numbers for the additional basis functions and find the minimum of the total energy of Pt_2 as function of the degree of ionization. In the third step we fixed the partial occupation numbers for these two basis sets and optimized the additional basis functions $5f5/2$ and $5f7/2$ in the same way as the $6p$ shell basis functions. In this way we increased the number of basis functions subshell by subshell until the total energy change by further increase of the number of basis functions was smaller than 0.01 eV. In total we used the minimal basis plus $6p1/2$, $6p3/2$, $5f5/2$, $5f7/2$, $5g7/2$, $5g9/2$, $6d3/2$, $6d5/2$, $6f5/2$, and $6f7/2$ optimized functions. In order to check whether this procedure leads to convergence of the correct total energy, we also generated the basis for Li_2 for which FEM (finite elements method) values are available [23] using this procedure. Our value for the total energy [20] is in very good agreement with the FEM value.

Table I shows the bond energies, bond length, and vibrational frequencies which we calculated from the Morse potential [24] fitted to our calculated values of the potential energy curve including the asymptotic value for Pt_2 for different exchange-correlation functionals. For every combination we performed a non-spin-polarized, a spin-polarized but collinear (SP), and a spin-polarized noncollinear (SP,non) calculation. From an analysis of the occupied orbitals on the minimum of the potential curve we can see that the system has no open spins and therefore it behaves in the calculation around the minimum of the potential energy curve as a closed shell system. This means that we get essentially the same total molecular energies for all three forms. This can be seen from the very little change in the bond distance and the vibrational frequencies. The mean change in the bond energy comes from the larger total energy of the molecular system at very large internuclear distances. In other words, the difference comes from the atomic calculations for the open shell system of the Pt atom. This agrees with other calculations with and without spin polarization [25]. We determinated the total energy of the Pt atom by calculating the Pt_2 molecules at large internuclear distances (> 40 a.u.). The calculations of the Pt atom with our molecule program using the same grid (counterpoints method) as used in the molecular calculations on the minimum of the potential curve give a difference which is much smaller then the uncertainty in the total energy due the final number of used basis functions. The magnetization density even in the molecular calculations at internuclear distances around the minimum was not zero everywhere in the space. But it was distributed in such a way that it essentially did not contribute to the very integral quantity: the total energy. In contrast to this in the calculations at large internuclear distances magnetization density is not only nonzero but also leads to changes in the total energy.

Recently the total energies for all atoms in the periodic table for several density functionals with spin polarization in their collinear form were published [26]. In our self-consistent, molecular calculation the total energy of the Pt atom for the nonrelativistic LDA was 18436.4981 hartree which is only 1.2 mhartree smaller than from [26]. We think the difference is due to the spherical average of the total density and the magnetization density in [26], whereas in our calculation the angular dependent density is used.

One can see from Table I that the LDA always gives slightly too short bond lengths, the largest bond energies, and, because of that, also the highest vibrational frequencies. The very simple X_α functional can reproduce all three quantities much better. Both Perdew-Wang [5] and Becke [6]-Perdew [7] combinations of exchange-correlation functionals in their noncollinear form reproduce the experimental result quite well.

A comparison of the experimental results with those from the many body theories shows quite large discrepancies in the ground states properties of Pt_2. We think that the reason for these relatively poor results is the too small active space set which cannot adequately represent the contribution of the $5d$ shell of the Pt to the bond of the Pt dimer. The difference between our calculations and the calculations from literature could be explained by the too small basis sets chosen and/or by the different form of the density functionals [9,10].

Using the GGA density functionals in their noncollinear form in combination with a fully relativistic description it is possible to calculate the ground-state properties for open shell systems. As a summary, one can say that the fully relativistic density functional calculations using the Becke 88 and Perdew 86 GGAs and with the noncollinear treatment of the spin magnetization lead to very good results which are, in the case of Pt_2, even superior to *ab initio* quantum chemical data.

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