

Noncollinear and collinear relativistic density-functional program for electric and magnetic properties of molecules

J. Anton and B. Fricke

Institut für Physik, Universität Kassel, D-34109 Kassel, Germany

E. Engel

Institut für Theoretische Physik, J. W. Goethe Universität Frankfurt, D-60054 Frankfurt am Main, Germany

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We present the general theory of the collinear and noncollinear description for the magnetic effects within the full relativistic density-functional method. As examples for the implementation in a molecular code with numerical basis functions we present results with an even number of electrons (Pt_2) and with an odd number of active electrons (NiAu). The results are promising.

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I. INTRODUCTION

The quick development of computational methods in Physics and Chemistry nowadays allows us to calculate energies and other properties of atoms, molecules, and small clusters with *ab initio* methods. In the first place these are “classical” but still very popular methods in quantum chemistry such as the Hartree-(Dirac-)Fock methods [1–3], configuration interaction, multiconfiguration Dirac-Fock, second order Møller-Plesset (MP2) [4], coupled cluster single double (triple) excitation [CCSD(T)] [5–8], and so on. The great advantage of all these methods is the possibility to achieve the “exact” solution (within the chosen method) just by increasing the number of configurations. Unfortunately this number increases as power of 4, 5, or even 7 with the number of active electrons, so that all these methods fight with the limit of the memory and central processing unit (CPU) power. Therefore these methods can nowadays only be applied to systems with relatively small numbers of active electrons such as atoms, small molecules, and small clusters. The results achieved for these systems are very good and serve as benchmarks. In the last two decades, however, many computational improvements are made to make these methods more efficient. With some approximations, for example, it was possible to achieve first a quadratic [9,10] and later on even a linear [11,12] scaling for the Hartree-Fock method. A linear scaling has been also achieved for the MP2 [13,14] as well as for the CCSD(T) [15] methods. This scaling behavior behind the high accuracy makes them very attractive also for large systems.

In 1964 Hohenberg and Kohn [16] were able to show that the total energy of any system in an external field can be described by a functional of its density only. This pioneer work is the basis of the density-functional theory (DFT) and provides an incentive for many theoreticians to find this functional. In the last three decades many approximations for the energy density functional were made which gave quite good results, but the exact form of the functional is still unknown.

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 [17,18] and ends with a fully relativistic description. A comparison of these approximations and corresponding results can be found in Refs. [19,20].

In the last three decades a series of different approximations for the exchange and correlation functionals were introduced. An overview can be found in Refs. [21,22]. All these functionals can be written either in relativistic or nonrelativistic form [23]. The two forms lead to different total energies, but almost the same bond energies and bond lengths in the case of molecules [19]. Therefore we will not distinguish between these two forms and the results for one form also represent 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 forms [24]. In a relativistic description the spin should actually be included in the relativistic form of the density functionals, which directly depends on the four current density [25,26], 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 theoretically consistent way via the magnetization density using a fictitious external magnetic field which is set to zero in the end formulas (for more details see Refs. [21,22]). In this case the exchange and/or correlation functionals depend not only on the density but also on the magnetization density (see details in Refs. [21,22,27]). The magnetization density at any point in space is defined as magnetic moment per volume [28]. 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. There are only a few implementations of the noncollinear approximations for atoms and solids known in the literature [27,29,30]. Only one of them reports an imple-

mentation for molecules where the authors used a scalar-relativistic description [31]. In a recent paper [32] we were able to present the first four-component implementation of the noncollinear density functionals for the diatomic molecule Pt₂. There is also a very recent report about a new full relativistic implementation [33].

In this paper we present a detailed description of the method to describe the magnetic effects. As the only other example in this paper in addition to the homonuclear molecule Pt₂, we present results for the heteronuclear system NiAu with an odd number of electrons which lead to a drastic effect of the noncollinear description in the molecule itself. Our theoretical values calculated with the noncollinear approximation are as good as the ones for Pt₂. In the Appendix details are presented for the calculation of the Hartree potential within this program.

II. METHOD

Starting from QED Rajagopal and Callaway [25] were able to prove that the ground-state energy is an unique functional of the ground-state four current and introduced a functional for the relativistic electron gas. Practical experience has shown that the functionals which depend on the density only cannot reproduce the experimental results [19,20]. One of the reasons was that the three-dimensional current for a relativistic electron gas is zero, and therefore these functionals cannot describe the system with internal magnetic field properly. One can rewrite the functional using the Gordon decomposition as functional dependent on the density and magnetization density. In the Gordon decomposition the three-dimensional current is represented as the sum of the orbit current and the magnetization. The first term is usually neglected because in most cases it is small in comparison to the second one. A general derivation can be found in Refs. [21,22]. One can prove [21,22] that the ground-state energy is an unique functional of the ground-state density ρ and magnetization density \vec{m} , provided the system is not subject to an external magnetic field. This means that the system can be completely described by its density and magnetization density.

Within this method the total energy of a molecular system is given by the expression

$$E = \sum_{i=1}^M n_i \langle \psi_i | \hat{t} | \psi_i \rangle + \int V^N \rho d^3\vec{r} + \frac{1}{2} \int V^H \rho d^3\vec{r} + E^{xc}[\rho, \vec{m}] + \sum_{p>q} \frac{Z_p Z_q}{|\vec{R}_p - \vec{R}_q|}, \quad (2.1)$$

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

$$\rho(\vec{r}) = \sum_{i=1}^M n_i \psi_i^\dagger(\vec{r}) \psi_i(\vec{r}), \quad (2.2)$$

$$\vec{m}(\vec{r}) = -\mu_B \sum_{i=1}^M n_i \psi_i^\dagger(\vec{r}) \beta \vec{\Sigma} \psi_i(\vec{r}). \quad (2.3)$$

Here n_i are the occupation numbers, \vec{r} and \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)

$$\hat{t} = c \vec{\alpha} \cdot \vec{p} + c^2(\beta - I), \quad (2.4)$$

where $\vec{\alpha} = (\alpha_x, \alpha_y, \alpha_z)$ and β are the four-component Dirac matrices in the standard representation [34] and I is the four-component unit matrix.

V^N is the nuclear potential

$$V^N = \sum_p -\frac{Z_p}{|\vec{r} - \vec{R}_p|}, \quad (2.5)$$

where the index p runs over all nuclei in the molecular system.

E^{xc} is the exchange-correlation energy functional. V^H is the electronic Hartree potential

$$V^H(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}'. \quad (2.6)$$

Since the calculation of the Hartree potential from the SCF density (2.2) is very time consuming, we approximate ρ in Eq. (2.2) 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 Hartree energies calculated from the difference of the SCF density ρ and model density $\tilde{\rho}$. This procedure leads to small corrections to the total energy (2.1) which are no longer linear, but quadratic in the difference $\rho - \tilde{\rho}$ [35]. We also emphasize that only the procedure described here has this property. All other similar methods such as Mulliken [36,37], density fitting [38,39], or even direct projection methods [40], lead to errors in the total energy which are linear in the difference of densities. However, all methods converge to the right Hartree potential if the basis for the model density becomes more and more complete.

Another improvement of our method is the possibility to control and avoid the linear dependency of the fit-basis functions. We diagonalize the fit matrix in the symmetry-adapted basis and set the occupation numbers for all orthogonalized symmetry-adapted fit functions which have a small norm (length) explicitly to zero. All these improvements (for more details see Appendix) allow an accurate calculation of the Hartree energy as will be shown in Sec. II C.

The variation of the energy functional (2.1) leads to the relativistic Kohn-Sham (KS) equations in their general form for the molecular orbitals ψ_i

$$\left\{ \hat{t} + V^N + \tilde{V}^H + \frac{\delta E^{xc}[\rho, \vec{m}]}{\delta \rho} - \mu_B \beta \vec{\Sigma} \cdot \frac{\delta E^{xc}[\rho, \vec{m}]}{\delta \vec{m}} \right\} \psi_i = \epsilon_i \psi_i, \quad i = 1, \dots, M'. \quad (2.7)$$

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

A. Collinear case

The collinear approximation of DFT is widely used in practice and motivated by the nonrelativistic DFT, where the spin is a good quantum number if the spin-orbit coupling is neglected. In this approximation one defines spin-up and spin-down densities, and uses exchange-correlation functionals which depend on these densities. In the relativistic theory, however, the exchange-correlation functionals should depend on the density and the magnetization density. Unfortunately up till now only the exchange part of the relativistic local-density approximation (RLDA) [41] is known in this form. Practice shows that one can still use the exchange-correlation functionals in their nonrelativistic form for relativistic molecular calculations because the difference between the results achieved by using one form or another are small [42]. In order to be able to define the spin densities in the relativistic description (compare Ref. [31]) one assumes that the magnetization density at every point in the space is aligned to the symmetry (z) axis. In this case one can calculate from the total density and the magnetization densities the generalized spin densities [21,22]

$$\rho_{\pm}(\vec{r}) = \frac{1}{2} \left[\rho(\vec{r}) \mp \frac{1}{\mu_B} m_z(\vec{r}) \right] = \sum_{i=1}^M n_i \psi_i^{\dagger} \frac{1 \pm \beta \Sigma_z}{2} \psi_i. \quad (2.8)$$

Using these densities the KS equations (2.7) can be written in the form

$$\left\{ \hat{t} + V^N(\vec{r}) + \tilde{V}^H(\vec{r}) + \frac{1 + \beta \Sigma_z}{2} V_+^{xc}(\vec{r}) + \frac{1 - \beta \Sigma_z}{2} V_-^{xc}(\vec{r}) \right\} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \quad (2.9)$$

with

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

B. Noncollinear case

In noncollinear case the KS equations in their general form (2.7) should be solved. One problem appearing in this case is that the variation of the exchange-correlation functionals $\delta E^{xc}[\rho, \vec{m}]/\delta \vec{m}$ is only known for the relativistic exchange-only LDA. On the other hand, it is well known that this functional describes all electronic systems much worse than the GGA's (general gradient approximation). In general these functionals should be extended to functionals which

are dependent on the density as well as on the magnetization density. The nonrelativistic form of the GGA's cannot be used because these are dependent on the spin densities, and because from a magnetization density which is not aligned to an axis these densities cannot be calculated. The simplest solution of this dilemma is to describe the system at each point in the space in a frame where the magnetization is parallel to z axis. This could be done by rotation of the magnetization density at each point in space as long as it becomes aligned to the z axis [43]. Now it could be used to calculate the generalized spin densities and in a following step also the exchange-correlation potentials. These potentials include one part which is dependent only on the density and other part which is dependent on the magnetization density (internal magnetic field). In order to get the right exchange-correlation potential for Eq. (2.7) the last part should be rotated back. Since both rotations are made locally this procedure leads to the exact solution of the general equation (2.7). It is well known [34] that a rotation in a real space is equal to a rotation in the spin space. From practical point of view the last one has some advantages, therefore we adapted this type of rotation in our program and present it also in this paper.

We want to introduce a four-vector

$$S_0(\vec{r}) = \frac{1}{2} \sum_{i=1}^M n_i \psi_i^{\dagger} \beta \psi_i, \quad \vec{S}(\vec{r}) = \frac{1}{2} \sum_{i=1}^M n_i \psi_i^{\dagger} \beta \vec{\Sigma} \psi_i, \quad (2.10)$$

where the spin density \vec{S} is related to the magnetization density by expression

$$\vec{m} = -2\mu_B \vec{S}. \quad (2.11)$$

It is well known that for every four-vector, there is a corresponding spinor of order 2 [34] which is built from the components of this vector. In our case the matrix has the form

$$\underline{\underline{S}}(\vec{r}) = \begin{pmatrix} S_0 + S_z & S_x - iS_y \\ S_x + iS_y & S_0 - S_z \end{pmatrix}. \quad (2.12)$$

All rotations of the four-vector, which includes not only rotations in the real three-dimensional space but also rotations in the Minkovsky space, can also be represented as rotations in the spin space. In this paper we are only interested in rotations in the three-dimensional space, therefore a general transformation is given by the unitary matrix $\underline{\underline{U}}(\vec{r})$ [34]

$$\underline{\underline{U}}(\vec{r}) = \begin{pmatrix} \cos \frac{\beta}{2} e^{(i/2)(\alpha + \gamma)} & \sin \frac{\beta}{2} e^{-(i/2)(\alpha - \gamma)} \\ \sin \frac{\beta}{2} e^{(i/2)(\alpha - \gamma)} & \cos \frac{\beta}{2} e^{-(i/2)(\alpha + \gamma)} \end{pmatrix}. \quad (2.13)$$

Here α , β , and γ are Euler rotational angles. We can diagonalize the matrix (2.12) and determine these angles by us-

ing the transformation matrix (2.13). This means that we have to solve the matrix equation

$$\underline{\underline{S}}(\vec{r}) = \underline{\underline{U}}^\dagger(\vec{r}) \text{diag}(S'_+, S'_-) \underline{\underline{U}}(\vec{r}). \quad (2.14)$$

This matrix equation is equal to a system of linear equations

$$S_{11} = S'_+ \cos^2 \frac{\beta}{2} + S'_- \sin^2 \frac{\beta}{2},$$

$$S_{22} = S'_+ \sin^2 \frac{\beta}{2} + S'_- \cos^2 \frac{\beta}{2},$$

$$\text{Re} S_{12} = \frac{1}{2} \cos \alpha \sin \beta (S'_+ - S'_-),$$

$$\text{Im} S_{12} = -\frac{1}{2} \sin \alpha \sin \beta (S'_+ - S'_-). \quad (2.15)$$

We want to denote that the rotation angle γ does not appear in these equations and therefore can be chosen arbitrarily. This is due to the rotational symmetry of the magnetization density with respect to the new z' axis. In order to simplify the end expressions we set this rotational angle to zero. The solution of this system has the form

$$\tan \alpha = -\frac{\text{Im}(S_{12})}{\text{Re}(S_{12})},$$

$$\tan \beta = 2 \frac{|S_{12}|}{S_{11} - S_{22}},$$

$$S'_+(\vec{r}) = \left(S_{11} \cos^2 \frac{\beta}{2} - S_{22} \sin^2 \frac{\beta}{2} \right) / \cos \beta,$$

$$S'_-(\vec{r}) = \left(S_{22} \cos^2 \frac{\beta}{2} - S_{11} \sin^2 \frac{\beta}{2} \right) / \cos \beta. \quad (2.16)$$

The eigenvalues of the matrix (2.12) are connected to the components of the four-vector by the expression

$$S'_0 = \frac{1}{2}(S'_+ + S'_-), \quad S'_z = \frac{1}{2}(S'_+ - S'_-). \quad (2.17)$$

We want to point out that in contrast to the nonrelativistic case the sum of eigenvalues ($2S'_0$) does not give the total density of the system. This is due to the presence of the small components and reflects the fact that a relativistic system cannot be completely spin polarized because the spin of a particle (an electron) is not a good quantum number in the relativistic description. Using the expression (2.17) for the z component of the spin density in the rotated system one can calculate the spin-up and the spin-down densities

$$\rho_\pm(\vec{r}) = \frac{1}{2} \{ \rho(\vec{r}) \mp [S'_+(\vec{r}) - S'_-(\vec{r})] \}. \quad (2.18)$$

Now we are able to calculate the exchange correlation potentials v_+^{xc} and v_-^{xc} using the generalized spin densities. To determine the exchange-correlation potential in the nonrotated system we can either make a rotation back in the spin space

$$\underline{\underline{V}}^{xc}(\vec{r}) = \underline{\underline{U}}^\dagger(\vec{r}) \text{diag}(v_+^{xc}, v_-^{xc}) \underline{\underline{U}}(\vec{r}), \quad (2.19)$$

which has the form

$$\underline{\underline{V}}^{xc}(\vec{r}) = \begin{pmatrix} v_+^{xc} \cos^2 \frac{\beta}{2} + v_-^{xc} \sin^2 \frac{\beta}{2} & \frac{1}{2} \sin \frac{\beta}{2} e^{-\alpha} (v_+^{xc} - v_-^{xc}) \\ \frac{1}{2} \sin \frac{\beta}{2} e^{-\alpha} (v_+^{xc} - v_-^{xc}) & v_+^{xc} \sin^2 \frac{\beta}{2} + v_-^{xc} \cos^2 \frac{\beta}{2} \end{pmatrix}, \quad (2.20)$$

or rotate the four-vector $B_\nu = (\frac{1}{2}(v_+^{xc} + v_-^{xc}), 0, 0, \frac{1}{2}(v_+^{xc} - v_-^{xc}))$ in real three-dimensional space. It is interesting to note that the internal magnetic field of a system and the “normal” exchange correlation potential are not independent of each other because both together build a four-vector. This fact is not important for this noncollinear case where only rotations in the three-dimensional space are involved. But if also Lorentz transformations are involved which correspond to a rotation in the four-dimensional space and involve also the time coordinate then this fact becomes very important.

After the rotation we get for the internal magnetic field

$$\vec{B}(\vec{r}) = \{ \frac{1}{2}(v_+^{xc} - v_-^{xc}) \cos \alpha \sin \beta, \frac{1}{2}(v_+^{xc} - v_-^{xc}) \cos \alpha \sin \beta, \frac{1}{2}(v_+^{xc} - v_-^{xc}) \cos \beta \}. \quad (2.21)$$

We want to stress again that all these steps are performed at each point in space, and therefore the solution which we achieve in this way is a exact solution of the general equation (2.7).

C. Test of the completeness of the atomic basis sets and of the accuracy of the Hartree energy

The relativistic Kohn-Sham equations in the noncollinear form (2.7) were solved by using numerical atomic orbitals as basis functions by the molecular orbital—linear combination of atomic orbitals method. The advantage of this method is the small number of basis functions which are required to achieve high accuracy by solving the many-centers Kohn-Sham equations. In this section we would like to show that the minimal basis plus only four to five additional basis functions lead to a final basis set error in the total energy of down to 0.01 eV only.

Besides this final basis set error there is also an error in the calculation of the Hartree potential (energy) \vec{V}^H in Eq. (2.7). As is described in the Appendix we use for the calculation of the Hartree potential a model density which is expanded into multicenter multipolar fit-basis functions. Generally speaking these can be chosen independently from the basis for the wave functions. However our experience shows that this leads to larger errors than if the same basis functions are applied. Due to this fact we use as fit functions the radial subshell densities multiplied by spherical harmonics up to a maximal number l_{max} which can be defined at the beginning

TABLE I. Total energies of Li_2 for different basis sets. All calculations are performed with relativistic kinetic energy and X_α exchange-energy functional.

Basis no.	Basis functions	Total energy (a.u.)
1	$1s_{1/2}, 2s_{1/2}$ neutral	-14.5397640
2	Basis no. 1 + $2p_{1/2}, 2p_{3/2}$ ($\text{Li}^{1.2+}$)	-14.5484306
3	Basis no. 2 + $3s_{1/2}, 3p_{1/2}, 3p_{3/2}$ ($\text{Li}^{1.3+}$)	-14.5491881
4	Basis no. 3 + $3d_{3/2}, 3d_{5/2}$ ($\text{B}^{3.2+}$)	-14.5492755
5	Basis no. 4 + $4s_{1/2}, 4p_{1/2}, 4p_{3/2}$ ($\text{B}^{2.9+}$)	-14.5496747
6	Basis no. 5 + $5s_{1/2}, 5p_{1/2}, 5p_{3/2}$ ($\text{N}^{5.1+}$)	-14.5498011
7	Basis no. 6 + $6s_{1/2}, 6p_{1/2}, 6p_{3/2}$ ($\text{O}^{5.8+}$)	-14.5498077
8	Basis no. 7 + $4f_{5/2}, 4f_{7/2}$ $\text{Ne}^{5.75+}$	-14.5498127
9	Basis no. 8 + $7s_{1/2}, 7p_{1/2}, 7p_{3/2}$ ($\text{Ne}^{8.2+}$)	-14.5498187
[46]	FEM	-14.5498278

of the calculation. Therefore a basis set optimization minimizes both the final basis set and Hartree-energy error.

In order to achieve the basis set optimization we start with numerical minimal basis functions for a neutral atom [44]. In the second step, we add basis functions of the next subshell from a calculation of an atom with a defined degree of ionization (we use noninteger occupation numbers). We make several molecular calculations with different partial occupation numbers for the additional basis functions and find the minimum of the total energy of dimer as function of the degree of ionization. In the third step, we fix the partial occupation numbers for these two basis sets and optimize the additional basis functions of the next subshell in the same way as the previous subshell. In this way we increase 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 a chosen value.

In order to test the accuracy of the Hartree energy we study the dependence of the total energy as function of the basis functions. The only basis-independent (FD [45], e.g., FEM [46]) reference value which we found was the value for Li_2 . In the first step, we increase successively the number of the basis functions. By using this optimization procedure we find the degrees of ionization listed in Table I. As it can be seen from this table, the total energy converges quite fast with increasing number of basis functions to the exact value.

In the second step, we study the dependence of the total energy on the maximal angular momentum quantum number l_{max} in the model density in Eq. (A1). The results of this study are collected in Table II where we present the results for the smallest and the biggest basis sets only. We can see a very rapid convergence of the total energy with the maximal

multipole moment. In most cases it is sufficient to use the contributions up to the quadrupole term in the model density.

One also observes a nearly constant difference between the values for the same multipoles for the two basis sets shown here. This means that the error from the incompleteness of the basis never will be compensated by use of higher multipole moments.

In addition we should mention that wave functions like $3d_{3/2}$ or $4f_{7/2}$ which have a structure in the angular part of the wave functions but no nodes in the radial part give a small contribution to the total energy or even can lead to worse results. This is due to the increased linear dependency of the basis functions. To avoid this in the fit procedure we use a method described also in the Appendix. In this method we have a cut parameter [see Eq. (A21)] which, generally speaking, can influence the results of the calculation. We also study the dependency of the total energy from this cut parameter and find that the change in the total energy for cut parameters between 10^{-4} – 10^{-6} are much smaller than the other errors discussed above. This means that for this choice of the cut parameter the linear dependency of the fit-basis set is reduced while the basis is still sufficiently large to represent the SCF density quite well. A cut parameter outside this interval makes the set too small (bigger ϵ values) or too linear dependent (small values). In both cases the final result becomes worse. We use in our calculation a value 10^{-5} .

As summary of these more technical but important details we can say that the approximations together with the optimization procedure work quite well. This allows one to calculate the total energies of molecular systems with accuracies below 0.01 eV and all differences above this limit are due to

TABLE II. Total energies of Li_2 for different basis sets as a function of angular momenta quantum number which was used in the calculation of the Hartree energy.

Basis no.	Monopole	Dipole	Quadrupole	Octupole
1	-14.5411696	-14.5398017	-14.5397934	-14.5397640
9	-14.5744133	-14.5499900	-14.5498213	-14.5498187

TABLE III. Ground-state properties of the homonuclear molecule Pt_2 and heteronuclear open-shell molecule NiAu . The abbreviation RLDA means the relativistic local density approximation for exchange only [23], B88 means the exchange only functional from Becke [47], P86 means the correlation functional from Perdew [48], and VWN means the correlation functional from Vosko *et al.* [49].

Molecule Reference	Method	NiAu			Pt ₂		
		D _e (eV)	R _e (a.u.)	ω (cm ⁻¹)	D _e (eV)	R _e (a.u.)	ω (cm ⁻¹)
This work	RLDA/VWN (SP)	4.30	3.16	315	4.19	4.35	239
This work	RLDA/VWN (SP,non)	4.30	3.16	317	4.00	4.35	235
This work	B88/P86 (SP)	4.43	2.49	280	3.28	4.42	225
This work	B88/P86 (SP,non)	4.44	2.49	276	3.12	4.42	224
[53], [50]	Expt.	4.443±0.002	2.52±0.17		3.14±0.02	4.40867 (83)	222.46±0.66

the choice of the density functionals and thus the method itself.

III. RESULTS AND DISCUSSION

A. Homonuclear molecular closed-shell system Pt_2

Table III shows the bond energies, bond length, and vibrational frequencies for Pt_2 . A comparison between different theoretical methods can be found in Refs. [32] and [50].

We calculated vibrational frequencies from the Morse potential [51] 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 spin-polarized collinear (SP) and a spin-polarized noncollinear (SP,non) calculation. From an analysis of the occupied orbitals at 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. From this the ground state of the Pt_2 molecules should be an O_g state, presumable translating to $^1\Sigma$. Due to this fact 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 [52]. We determined the total energy of the Pt atom by calculating the Pt_2 molecule at large internuclear distances (>40 a.u.). The calculations of the Pt atom with our molecular program using the same grid as used in the molecular calculations at the minimum of the potential curve give a difference which is much smaller than the uncertainty in the total energy due to the final number of basis functions used.

B. Heteronuclear molecular open-shell system NiAu

In order to test the calculational method which we discuss here we have chosen one of the few experimentally known [53] heteronuclear diatomic molecules with an odd number of electrons, at least one nd hole, and where at least one atom is very heavy: NiAu .

We optimized the basis functions in the way as it is described in the preceding section for the Ni_2 and Au_2 systems

separately. Using these basis sets we performed the calculations for NiAu . Our results are collected in Table III. As it is already shown the case for Pt_2 the GGA results (B88/P86) in combination with the spin polarization can reproduce very well the bond length as well as the bond energies for this open-shell molecule.

From the experimental data it is known that the ground state of NiAu is a $^2\Delta_{5/2}$ state. We performed some analysis in order to figure out the symmetry of the system from our calculations. The integral over the magnetization density gives us per definition the total magnetic moment of the molecular system which correlates to the total spin of the system. We found that the total spin of this molecular system is $S=1/2$, in agreement with experimental observation. From an analysis of the occupied orbitals (see below) we estimated the ground state symmetry of the NiAu molecule as $^2\Delta_{5/2}$ which agrees with the experimental determined one.

In the experimental paper [53] the authors predicted the ground-state configuration of this molecule to be $d_{\text{Ni}}^9 d_{\text{Au}}^{10} \sigma^2$. To find evidence for this we looked to the expansion coefficients of the occupied molecular orbitals. Due to the large overlap of the $4s_{\text{Ni}}, 3d_{\text{Ni}}$ and $6s_{\text{Au}}, 5d_{\text{Au}}$ all these orbitals were far away from ‘‘pure’’ atomic states. In most cases more than two atomic orbitals contributed to the outer molecular orbitals. When we looked to the leading term in each expansion we found that both $4s$ orbitals as well as the $3d_{5/2}$ orbital from Ni are unoccupied. From the Mulliken overlap population analysis we additionally found that the first two correspond to the antibonding σ orbitals and the last one to the antibonding $d\delta$ state. From the overlap population analysis we also can see that all molecular orbitals formed from the d orbitals of both atoms of the NiAu molecule do not have well-pronounced bonding or antibonding character. This agrees with the assumption of the experimentalists [53]. In order to check how good this assumption works we performed the Mulliken analysis to estimate the electron distribution in the molecule. These are presented in Table IV. One can see some charge transfer from the $4s_{1/2}$ to $3d$ subshell of Ni. One can also see that the d hole resides mostly on nickel site. This means that the assumption made by the experimentalists about the ground state of the NiAu molecule are quite good.

C. Conclusion

As summary one can say that we have been able to calculate two very different diatomic molecules. This makes us

TABLE IV. Mulliken occupation numbers for the heteronuclear open-shell molecule NiAu at the bound distance.

Basis type	Occupation	Basis type	Occupation
Ni minimal basis		Au minimal basis	
$1s_{1/2}-3p_{3/2}$	17.9816976	$1s_{1/2}-5p_{3/2}$	68.0056798
$3d_{3/2}$	3.6251786	$5d_{3/2}$	3.9263932
$3d_{5/2}$	5.3712440	$5d_{5/2}$	5.7907258
$4s_{1/2}$	0.9061068	$6s_{1/2}$	1.0887852
Sum minimal basis	27.8842268	Sum minimal basis	78.8115840
Additional basis	0.2890275	Additional basis	0.0151617
Total	28.1732543	Total	78.8267457

hopeful that calculations of larger molecules will lead to accurate results not only for the bond energies and distances but also for magnetic moments and magnetic moment distributions.

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APPENDIX: CALCULATION OF THE ELECTRONIC HARTREE POTENTIAL

Only for a single atom (one-center system) the calculation of the electronic Hartree potential (2.6) is relatively simple. In the multicenter case the calculation of this potential from the self-consistent density (2.2) is very difficult. Therefore usually an approximative Hartree potential is used [38,39]. We use a multipole, multicenter expansion of the molecular charge density. We approximate it by

$$\tilde{\rho}(\vec{r}) = \sum_{K=1}^{N_A} \sum_{j=1}^{M_K} \sum_{l=0}^{L_j} \sum_{m=-l}^l Q_{jm}^{Kl} F_K^j(\xi_K) Y_l^m(\theta_K, \phi_K). \quad (\text{A1})$$

Here $F_K^j(\xi_K) = [P_j^2(\xi_K) + G_j^2(\xi_K)]$ are the atomic shell densities which are built from the large P_j and small G_j components of the atomic wave functions, Y_l^m are the real spherical harmonics, and Q_{jm}^{Kl} are the occupation numbers. K runs over all atoms in the molecular system N_A , j runs over all shells in the atom K , and l runs over all angular momenta L_j of the shell j . Since the Hartree potential is linear in the density we can write it as a sum

$$V(\vec{r}) = \sum_{K=1}^{N_A} \sum_{j=1}^{M_K} \sum_{l=0}^{L_j} \sum_{m=-l}^l Q_{jm}^{Kl} \int \frac{F_K^j(\xi'_K) Y_l^m(\theta'_K, \phi'_K)}{|\vec{r} - \vec{r}'|} d^3\vec{r}'. \quad (\text{A2})$$

After the coordinate transformation (for coordinate definition see Fig. 1) we get

$$V(\vec{r}) = \sum_{K=1}^{N_A} \sum_{j=1}^{M_K} \sum_{l=0}^{L_j} \sum_{m=-l}^l Q_{jm}^{Kl} \int \frac{F_K^j(\xi'_K) Y_l^m(\theta'_K, \phi'_K)}{|\vec{\xi}_K - \vec{\xi}'_K|} d^3\vec{\xi}'_K. \quad (\text{A3})$$

We can rewrite the term $1/|\vec{\xi}_K - \vec{\xi}'_K|$ by using the Legendre polynomials $P_{l'}(\cos \omega_K)$ in the form

$$\frac{1}{|\vec{\xi}_K - \vec{\xi}'_K|} = \begin{cases} \sum_{l'=0}^{\infty} \frac{\xi_K^{l'}}{\xi_K^{l'+1}} P_{l'}(\cos \omega_K) & \xi_K \geq \xi'_K \\ \sum_{l'=0}^{\infty} \frac{\xi_K^{l'}}{\xi_K^{l'+1}} P_{l'}(\cos \omega_K) & \xi_K < \xi'_K. \end{cases} \quad (\text{A4})$$

If we replace the Legendre polynomials $P_{l'}$ by real spherical harmonics $Y_{l'}^{m'}$,

$$P_{l'}(\cos \omega_K) = \frac{4\pi}{2l'+1} \sum_{m'=-l'}^{l'} Y_{l'}^{m'}(\theta_K, \phi_K) Y_{l'}^{m'}(\theta'_K, \phi'_K) \quad (\text{A5})$$

we can rewrite Eq. (A4) in the form

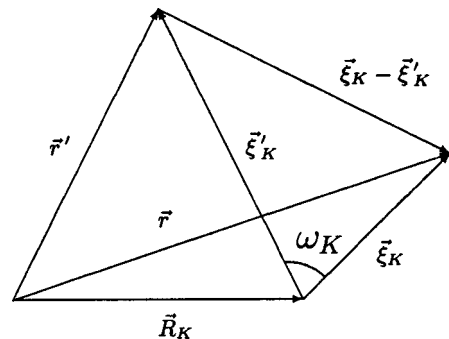


FIG. 1. Electronic coordinates in molecular (\vec{r}, \vec{r}') and atomic ($\vec{\xi}_K, \vec{\xi}'_K$) frame. \vec{R}_K is the displacement vector of the atom K .

$$\frac{1}{|\tilde{\xi}_K - \tilde{\xi}'_K|} = \begin{cases} \sum_{l'=0}^{\infty} \frac{\xi'^{l'}}{\xi_K^{l'+1}} \frac{4\pi}{2l'+1} \sum_{m'=-l'}^{l'} Y_{l'}^{m'}(\theta_K, \phi_K) Y_{l'}^{m'}(\theta'_K, \phi'_K), & \xi_K \geq \xi'_K, \\ \sum_{l'=0}^{\infty} \frac{\xi_K^{l'}}{\xi'^{l'+1}} \frac{4\pi}{2l'+1} \sum_{m'=-l'}^{l'} Y_{l'}^{m'}(\theta_K, \phi_K) Y_{l'}^{m'}(\theta'_K, \phi'_K), & \xi_K < \xi'_K. \end{cases} \quad (\text{A6})$$

If we insert this in Eq. (A2) and integrate over the angular coordinates and take into account the orthogonality of the spherical harmonics

$$\int d\Omega'_K Y_l^m(\theta'_K, \phi'_K) Y_{l'}^{m'}(\theta'_K, \phi'_K) = \delta_{ll'} \delta_{mm'}, \quad (\text{A7})$$

we get the formula [39]

$$\begin{aligned} \tilde{V}(\vec{r}) = & \sum_{K=1}^{N_A} \sum_{j=1}^{M_K} \sum_{l=0}^{L_j} \sum_{m=-l}^l \frac{4\pi Q_{jm}^{Kl}}{2l+1} Y_l^m(\theta, \phi) \\ & \times \left[\frac{1}{\xi_K^{l+1}} \int_0^{\xi_K} d\xi' \xi'^{l+2} F_K^j(\xi') \right. \\ & \left. + \xi_K^l \int_{\xi_K}^{\infty} d\xi' \xi'^{l-1} F_K^j(\xi') \right]. \end{aligned} \quad (\text{A8})$$

1. Fit of the molecular density

In order to simplify the following discussion we introduce new occupation numbers and fit-basis functions

$$q_\nu = Q_{jm}^{Kl}, \quad \varphi_\nu = F_K^j(\xi_K) Y_l^m(\theta_K, \phi_K), \quad (\text{A9})$$

where ν represents any combination of the indices (K, j, l, m) . In the new basis Eq. (A1) can be rewritten in the form

$$\tilde{\rho}(\vec{r}) = \sum_{\nu} q_{\nu} \varphi_{\nu}. \quad (\text{A10})$$

To determine the occupation numbers q_{ν} we use the least-square fit method [38]. We minimize the Hartree energy [54] calculated from the difference of the SCF density and model density [35]

$$\int \int \frac{[\rho(\vec{r}) - \tilde{\rho}(\vec{r})][\rho(\vec{r}') - \tilde{\rho}(\vec{r}')]}{|\vec{r} - \vec{r}'|} d^3\vec{r} d^3\vec{r}' = \min. \quad (\text{A11})$$

Inserting Eq. (A10) into Eq. (A11) we get

$$\int \int \frac{\left(\rho(\vec{r}) - \sum_{\nu} q_{\nu} \varphi_{\nu}(\vec{r})\right) \left(\rho(\vec{r}') - \sum_{\nu} q_{\nu} \varphi_{\nu}(\vec{r}')\right)}{|\vec{r} - \vec{r}'|} d^3\vec{r} d^3\vec{r}' = \min. \quad (\text{A12})$$

We vary this functional by preservation of multipole moments. In practice we normally use the first two—monopole moment Q and dipole moment \vec{d} ,

$$\sum_{\nu} q_{\nu} \int \varphi_{\nu} d^3\vec{r} = Q, \quad \sum_{\nu} q_{\nu} \int \vec{r} \varphi_{\nu} d^3\vec{r} = \vec{d}. \quad (\text{A13})$$

These constraints can be included in the variation by the standard Lagrange multiplier technique [55]. After the variation of q_{ν} and λ we get the matrix equation

$$\underline{\underline{A}} \underline{\underline{x}} = \underline{\underline{b}}, \quad (\text{A14})$$

with

$$A_{\mu\nu} = \int \int \frac{\varphi_{\mu}(\vec{r}) \varphi_{\nu}(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r} d^3\vec{r}',$$

$$\underline{\underline{x}} = \{q_{\nu}, \lambda_i/2\},$$

$$b_{\nu} = \int \int \frac{\rho(\vec{r}) \varphi_{\nu}(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r} d^3\vec{r}',$$

$$\underline{\underline{b}} = \{b_{\nu}, Q, d_x, d_y, d_z\}. \quad (\text{A15})$$

In principle Eq. (A14) solves the problem of the determination of the fit occupation numbers.

2. Symmetry-adapted basis

A major disadvantage of Eq. (A14) is that by solving it the symmetry of the molecular system cannot be used. In order to improve this we use symmetry-adapted basis functions ϕ_k which we expand in a series of the atomic basis function φ_ν

$$\phi_k = \sum_\nu C_{\nu k} \varphi_\nu. \quad (\text{A16})$$

Here ($C_{\nu k}$)'s are the symmetry coefficients which can be determined from group-theoretical properties of the molecular system [56]. In the new basis the \underline{A} matrix gets a block structure [57] with only one full symmetric representation

$$\underline{A} = \begin{pmatrix} \square & & & \\ & \square & & \\ & & \square & \\ & & & \square \end{pmatrix}. \quad (\text{A17})$$

The density itself is fully symmetric, too. Therefore it has an overlap only with the basis functions from this symmetry block and is orthogonal to all other symmetry-adapted basis functions from other symmetry blocks. The matrix equation (A14) therefore has the form

$$\begin{pmatrix} \square & & & \\ & \square & & \\ & & \square & \\ & & & \square \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \end{pmatrix} = \begin{pmatrix} b_1 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \quad (\text{A18})$$

X_i means the part of the solution vector which corresponds to symmetry block i . b_1 are the overlap integrals between the molecular density and symmetry-adapted basis functions from the total symmetric block.

This matrix equation is split up into g (number of irreducible representations of the symmetry group) independent systems of linear equations. It is easy to see that only the system which corresponds to the fully symmetric representation gives a nontrivial solution. We therefore have to solve only

this system of linear equations to estimate the symmetry-adapted occupation numbers x_j . The back transformation to the atomic occupation numbers q_ν is given by the expression

$$q_\nu = \sum_j C_{j\nu} x_j. \quad (\text{A19})$$

3. Linear dependence of the atomic fit-basis functions

From the general point of view the ansatz (A10) is overcomplete. This can easily be verified if the number of the atomic fit-basis functions is infinite. In this case each atomic basis set builds a complete set of basis functions, so that we do not need the fit-basis functions from all other atoms and may therefore exclude them from the fit procedure. In the case of a finite number of basis functions this is not that obvious because a very small number of them can build an orthogonal basis set. But by increasing the number of basis functions the basis becomes more and more linear dependent, which could lead to numerical problems. In order to minimize these problems we use the following method which is analogous to the canonical method to solve the eigenvalue problems [58]. We diagonalize the A matrix in the symmetry-adapted basis

$$\underline{A} \underline{Y} = \underline{a} \underline{Y}. \quad (\text{A20})$$

The eigenvalues a_{ii} of this matrix are the norms (lengths) of the eigenvectors Y_i . The eigenvectors with the smallest length span a small part of the basis space. On the other hand, these vectors are very sensitive to numerical errors because by the normalization of them we have to divide by a very small number. Therefore we set the occupation numbers of eigenvectors with small length

$$a_{ii} < \epsilon \quad (\text{A21})$$

explicitly to zero and use these conditions as additional constraints in our variation problem, Eq. (A11). In the symmetry-adapted basis these constraints have the form

$$0 = \sum_j y_{ji} x_j. \quad (\text{A22})$$

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- [1] D.R. Hartree, Proc. Cambridge Philos. Soc. **24**, 89 (1928).
 [2] V. Fock, Z. Phys. **61**, 126 (1930).
 [3] C.C.J. Roothaan, Rev. Mod. Phys. **23**, 69 (1951).
 [4] C. Møller and M.S. Plesset, Phys. Rev. **46**, 618 (1934).
 [5] J. Čížek, Adv. Chem. Phys. **14**, 35 (1969).
 [6] G.D. Purvis and R.J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
 [7] J.A. Pople, M. Head-Gordon, and K. Raghavachari, Chem. Phys. **98**, 8718 (1993).
 [8] J.D. Watts, J. Gauss, and R.J. Bartlett, J. Chem. Phys. **98**, 8718 (1993).
 [9] M. Häuser and R. Ahlrichs, J. Comput. Chem. **10**, 104 (1988).
 [10] I. Panas, J. Almlöf, and M.W. Feyereisen, Int. J. Quantum Chem. **40**, 797 (1991).
 [11] M.C. Strain, G.E. Scuseria, and M.J. Frisch, Science **271**, 51 (1996).
 [12] C. Ochsenfeld, C.A. White, and M. Head-Gordon, J. Chem. Phys. **109**, 1663 (1998).
 [13] P.Y. Ayala and G.E. Scuseria, J. Chem. Phys. **110**, 3660 (1999).
 [14] M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999).
 [15] M. Schütz and H.-J. Werner, Chem. Phys. Lett. **318**, 370 (2000).
 [16] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).
 [17] E. van Lenthe, E.J. Baerends, and J.G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
 [18] E. van Lenthe, J.G. Snijders, and E.J. Baerends, J. Chem. Phys. **105**, 6505 (1996).

- [19] S. Varga, E. Engel, W.-D. Sepp, and B. Fricke, *Phys. Rev. A* **59**, 4288 (1999).
- [20] S. Varga, B. Fricke, H. Nakamatsu, T. Mukoyama, J. Anton, D. Geschke, A. Heitmann, E. Engel, and T. Baştuğ, *J. Chem. Phys.* **112**, 3499 (2000).
- [21] E. Engel, R.M. Dreizler, S. Varga, and B. Fricke, in *Relativistic Effects in Heavy-Element Chemistry and Physics*, edited by B.A. Hess (Wiley, New York, 2001).
- [22] E. Engel, in *Relativistic Electronic Structure Theory, Part I: Fundamentals*, edited by P. Schwerdtfeger (Elsevier, Amsterdam, 2002).
- [23] E. Engel and R.M. Dreizler, in *Density Functional Theory II*, edited by R.F. Nalewajski, Vol. 181 (Springer-Verlag, Berlin, 1996).
- [24] U. von Barth and L. Hedin, *J. Phys. C* **5**, 1629 (1972).
- [25] A.K. Rajagopal and J. Callaway, *Phys. Rev. B* **7**, 1912 (1973).
- [26] A.H. MacDonald and S.H. Vosko, *J. Phys. C* **12**, 2977 (1979).
- [27] H. Eschrig and V.D.P. Servedio, *J. Comput. Chem.* **20**, 23 (1999).
- [28] J.D. Jackson, in *Klassische Elektrodynamik* (de Gruyter, Berlin, 1983).
- [29] L. Nordström and D.J. Singh, *Phys. Rev. Lett.* **76**, 4420 (1996).
- [30] L.M. Sandratskii, *Adv. Phys.* **47**, 91 (1998).
- [31] C. van Wüllen, *J. Comput. Chem.* **23**, 779 (2002).
- [32] J. Anton, T. Jacob, B. Fricke, and E. Engel, *Phys. Rev. Lett.* **89**, 213001 (2002).
- [33] F. Wang and W.J. Liu, *J. Chin. Chem. Soc. (Taipei)* **50** (3B), 597 (2003).
- [34] L.D. Landau and E.M. Lifschitz, *Quantenelektrodynamik* (Akademie-Verlag, Berlin, 1986).
- [35] T. Baştuğ, D. Heinemann, W.-D. Sepp, D. Kolb, and B. Fricke, *Chem. Phys. Lett.* **211**, 119 (1993).
- [36] R.S. Mulliken, *J. Chem. Phys.* **23**, 1833 (1955).
- [37] R.S. Mulliken, *J. Chem. Phys.* **23**, 1841 (1955).
- [38] B.I. Dunlap, J.W.D. Connolly, and J.R. Sabin, *J. Chem. Phys.* **71**, 3396 (1979).
- [39] B. Delley and D.E. Ellis, *J. Chem. Phys.* **76**, 1949 (1982).
- [40] W. Liu and Ch. van Wüllen, *J. Chem. Phys.* **113**, 2506 (2000).
- [41] M.V. Ramana and A.K. Rajagopal, *J. Phys. C* **14**, 4291 (1981).
- [42] E. Engel, T. Auth, and R.M. Dreizler, *Phys. Rev. B* **64**, 235126 (2001).
- [43] This is so-called passive rotation (Ref. [34]). An active rotation, namely, the rotation of the coordinate system leads to the same result.
- [44] It is also possible to use basis functions for a slightly ionized atom. But this basis cannot be used for all internuclear distances because it cannot adequately represent the molecular system at large internuclear distances.
- [45] L. Laaksonen, D. Sundholm, and P. Pyykkö, *Comput. Phys. Rep.* **4**, 313 (1986).
- [46] L. Yang, D. Heinemann, and D. Kolb, *Phys. Rev. A* **48**, 2700 (1993).
- [47] A.D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- [48] J.P. Perdew, *Phys. Rev. B* **33**, 8822 (1986).
- [49] S.H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- [50] M.M. Airoola and M.D. Morse, *J. Chem. Phys.* **116**, 1313 (2002).
- [51] P.M. Morse, *Phys. Rev.* **34**, 57 (1929).
- [52] W. Liu and Ch. van Wüllen, *J. Chem. Phys.* **110**, 3730 (1999).
- [53] E.M. Spain and M.D. Morse, *J. Chem. Phys.* **97**, 4605 (1992).
- [54] This procedure can be also used to minimize the difference of the SCF density and model density.
- [55] P. Funk, *Variationsrechnung und ihre Anwendung in Physik und Technik* (Springer-Verlag, Berlin, 1970).
- [56] W. Ludwig and C. Falter, *Symmetries in Physics* (Springer-Verlag, Berlin, 1988).
- [57] Only matrix elements in the squares may be not equivalent to zero. All other are.
- [58] P.O. Löwdin, *Adv. Phys.* **5**, 51 (1956).