PHYSICAL REVIEW A VOLUME 37, NUMBER 3 FEBRUARY 1, 1988

Molecules in strong magnetic fields: Properties of atomic orbitals

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(Received 17 August 1987)

We establish a basis set of atomic orbitals suitable to describe molecular wave functions at arbitrary magnetic field strengths and for an arbitrary orientation of the molecule relative to the magnetic field. A simple calculation for the hydrogen atom demonstrates the superiority of such an orbital over common orbitals. All types of matrix elements of the Hamiltonian of a molecule in a strong magnetic field are evaluated within our basis set of atomic orbitals.

I. INTRODUCTION

The astrophysical discovery of strong magnetic fields on white dwarfs[1] ($\approx 10^7$ G) and on the surface of neutron stars ($\approx 10^{12}$ G) motivated many studies on the behavior of atoms in strong magnetic fields.[2–7] Of special interest were the ground state and first few excited states of the hydrogen atom, which were studied with increasing accuracy[8–14] and with methods valid over the whole range of magnetic field strengths.[13,14] The parameter which characterizes the high and low magnetic field region is given by the ratio of the cyclotron energy and the Coulomb binding energy. This means that already at the available laboratory magnetic field strengths ($\approx 10^6$ G) typical strong field effects can appear. Examples are the Rydberg atoms or the excitons in a semiconductor[15] for which, because of the small effective masses and large dielectric constants, the Rydberg energy is very small.

In contrast to the numerous studies on the hydrogen atom, the information about the behavior of many-electron atoms and, in particular, about molecules in strong magnetic fields is very scarce. In the case of molecules the knowledge is, in general, restricted to the H_2^+ ion.[16–24] Already for the H_2^+ ion in the ground state one encounters a richness of phenomena, like the contraction of bond distances, the enormous increase in binding energy, and the new nuclear equation of motion resulting in a kind of pendulum oscillation of the molecular axis.[21] Many more phenomena are to be expected for other molecules, in particular for those with electron-electron interaction. For the ground state of a molecule at equilibrium distance significant effects will appear only for strong magnetic fields. For the first few excited states (non-Rydberg) the typical strong-field effects will arise at some lower field strength.

The lack of a general method for calculating molecular electronic wave functions motivated us to search for a basis set of functions, suitable to describe electronic wave functions for every field strength, being guided by the common variational basis-set calculations of molecular systems in the absence of a magnetic field. In Sec. II we discuss the requirements a basis set of one particle functions should fulfill in a magnetic field. In the remaining part of the paper we present a method of calculating all kinds of matrix elements of the Hamiltonian within this basis set.

II. THE HAMILTONIAN AND THE SUITABLE ATOMIC ORBITALS

The Hamiltonian of a molecule in a strong magnetic field contains, in addition to the kinetic energy and the Coulomb-interaction operators, terms which are linear (i.e., which describe paramagnetism) and quadratic (i.e., which describe diamagnetism) in the magnetic field strength. One possible starting point for the calculation of molecular electronic wave functions is the choice of a suitable basis set of atomic orbitals. The next step is then the calculation of the matrix elements of the Hamiltonian with these atomic orbitals. With the aid of these matrix elements one subsequently constructs in the usual way the Hamiltonian matrix, the eigenvectors and eigenvalues of which are the approximate N-particle molecular wave functions, and the corresponding energies, respectively.

In the following we will carry out the first two steps, i.e., we will establish in this section a basis of atomic orbitals for molecules in a magnetic field and in Sec. III we will calculate the matrix elements of the Hamiltonian. The nonrelativistic electronic Hamiltonian in the infinite nuclear mass limit takes on the following appearance:

$$H=\sum_{i=1}^{N}\frac{1}{2m}\left[\mathbf{p}_i-\frac{e}{c}\mathbf{A}(\mathbf{r}_i)\right]^2+V(\{\mathbf{r}_i\},\{\mathbf{R}_k\}) , \quad (1)$$

where $\mathbf{p}_i,\mathbf{r}_i$ are the momentum and position of the ith electron, m and e are the mass and charge of the electron, $\mathbf{A}(\mathbf{r}_i)$ is the vector potential at the position of the ith electron, and $\mathbf{R}_k$ stands for the position vector of the kth nucleus. The potential $V(\{\mathbf{r}_i\},\{\mathbf{R}_k\})$ contains all the Coulomb-interaction terms. The trivial Zeeman-spin terms have been omitted. A frequently used gauge for $\mathbf{A}(\mathbf{r})$ in Eq. (1) is the symmetric or Coulomb gauge $\mathbf{A}(\mathbf{r})=\frac{1}{2}\mathbf{B}\times\mathbf{r}$, where $\mathbf{B}$ is a homogeneous magnetic field. This symmetric gauge can be obtained from the more general mixed gauge,

$$A_i(\mathbf{r})=(1-\rho_j)B_j x_k - x_j\rho_k B_k , \quad (2)$$

by setting the parameters (ρ_1,ρ_2,ρ_3) all equal to $\frac{1}{2}$. In Eq. (2) the notation $\mathbf{r}^T=(x_1,x_2,x_3)$ is chosen for convenience and (i,j,k) are cyclic permutations of (1,2,3).

Although the fixed-nuclei electronic Hamiltonian (1) is well defined, a few remarks concerning the range of its usefulness are in order. Equation (1) is formulated in relative coordinates to the center of mass. An exact separation of the center-of-mass motion cannot be carried out in general for the case of a molecule in an external magnetic field.[25–27] Nevertheless, there exists a symmetry of phase-space translations[25] which leads to a "new" conserved quantity called the pseudomomentum **k**,

$$\mathbf{k}=\sum_i \left[\mathbf{p}_i-\frac{e}{c}\mathbf{A}(\mathbf{r}_i)+\frac{e}{c}(\mathbf{B}\times\mathbf{r}_i)\right] +\sum_k \left[\mathbf{P}_k-\frac{e_k}{c}\mathbf{A}(\mathbf{R}_k)+\frac{e_k}{c}(\mathbf{B}\times\mathbf{R}_k)\right] . \tag{3}$$

$\mathbf{P}_k$ and e_k denote the momentum and charge of the kth nucleus. In coordinates related to the center of mass, the terms of the Hamiltonian depending on the total pseudomomentum look, for a neutral molecule, as follows:

$$\frac{\hbar^2\mathbf{k}^2}{2M}+\frac{\hbar\mathbf{k}}{M}(-e)\left[\mathbf{B}\times\sum_j \alpha_j\mathbf{r}_j\right] , \tag{4}$$

where M is the total mass of the molecule, α_j some real constants. The negligibility of the coupling of the total pseudomomentum to the internal degrees of freedom can be fully justified by a special experimental preparation which prefers $\mathbf{k}=0$ states. In the general case of $\mathbf{k}\neq 0$ states one can show the negligibility of the influence of these couplings by their estimation through perturbation theory. For ions there exist some recent calculations,[28,29] which indicate that for hydrogenic atomic ions the center of mass motion can be neglected below a magnetic field strength of 10^{10} G. As usual the effect of finite nuclear masses can be included[30] in (1) by replacing the electronic mass m by a reduced mass μ. This effect becomes important only above a magnetic field strength of 10^{10} G. Finally, we mention that the use of a pure electronic Hamiltonian such as (1) is only meaningful if the Born-Oppenheimer approximation, which separates the electronic and nuclear motion, is valid. The Born-Oppenheimer approximation for molecules in a magnetic field will be discussed in detail elsewhere.[31]

In the following we concentrate on the Hamiltonian (1). The Schrödinger equation with the Hamiltonian (1) is invariant with respect to the gauge transformations

$$\begin{aligned}&\mathbf{A}(\mathbf{r}_i)\rightarrow\mathbf{A}(\mathbf{r}_i)-\nabla_i\Lambda(\mathbf{r}_i) ,\\ &\Psi(\{\mathbf{r}_i\})\rightarrow\exp\left[-\frac{ie}{\hbar c}\sum_i\Lambda(\mathbf{r}_i)\right]\Psi(\{\mathbf{r}_i\}) ,\end{aligned} \tag{5}$$

with arbitrary $\Lambda=\Lambda(\mathbf{r}_i)$. We will now discuss the consequences of the gauge degrees of freedom on the variational principle and on the choice of atomic orbitals. The expectation value of the Hamiltonian (1) with respect to an arbitrary trial wave function depends in general on the gauge of the vector potential. If one calculates the current density with this trial function one obtains that the equation of continuity for charge conservation is, in general, not satisfied.[32,33] The gauge dependence of physical quantities such as magnetic susceptibilities and magnetic shieldings lead historically to the construction of the so-called "gauge invariant" atomic orbitals[34–36] given by

$$\Psi(\mathbf{r},\mathbf{R})=\exp\left[+\frac{ie}{\hbar c}\mathbf{A}(\mathbf{R})\mathbf{r}\right]\Phi(\mathbf{r}-\mathbf{R}) , \tag{6}$$

where Φ is some trial function independent of **A**. However, the function Ψ does not ensure gauge invariance in general.[37] The purpose of the phase in Eq. (6), rather, is to enforce the gauge centering of the atomic orbital (6) on the atom with the nuclear position **R**. As a consequence atomic orbitals of the type (6) describe the correct diamagnetism in the dissociation and united-atom limits. Nevertheless, functions of the type (6) still provide different energy expectation values for different gauges of the Hamiltonian (1).

To obtain the gauge-invariant energy one has to carry out a functional variation of the energy-expectation value with respect to Λ, i.e., one has to minimize the energy with respect to Λ.[32,33] The general variation with arbitrary Λ is only practicable for certain special Hamiltonians.[32] In the following we discuss the necessary modifications of the ansatz (6) to obtain atomic orbitals which ensure at least approximate gauge invariance. The first step is to use the functions

$$\Psi(\mathbf{r};\mathbf{R},\mathbf{C})=\exp\left[+\frac{ie}{\hbar c}\mathbf{A}(\mathbf{C})\mathbf{r}\right]\Phi(\mathbf{r}-\mathbf{R}) , \tag{7}$$

where **C** is a vector of variational parameters, determined by minimizing the energy-expectation value. The new gauge center **C**, in general, does not necessarily coincide with the nuclear position vector $\mathbf{R}_k$. The set of functions arising from (7) is able to describe minimal energy values with respect to the restricted class of gauge transformations[37]

$$\mathbf{A}(\mathbf{r})\rightarrow\mathbf{A}(\mathbf{r})+\nabla(\mathbf{A}(\mathbf{d})\mathbf{r}) , \tag{8}$$

where **d** is an arbitrary constant vector. The correct diamagnetic energies in the dissociation and united-atom limits are guaranteed by the fact that **C** coincides with the nuclear position vector in these limits, i.e., $\mathbf{C}\rightarrow\mathbf{R}$ for infinitely separated or united atoms.

So far we have not specified the gauge of the vector potential in Eq. (7). For the special case of a molecular system with cylindrical symmetry in a magnetic field (for example, a diatomic molecule with the nuclear axis parallel to the magnetic field direction), one would choose the symmetric gauge, because it provides the minimal, i.e., gauge-invariant, energy value.[33] In the general case one has to take the mixed gauge (2) for **A** in the ansatz (7) and minimize the energy with respect to the parameters (ρ_1,ρ_2,ρ_3). There exist indications that the obtained energy is very near to the gauge-invariant one.[21,32] After having presented the part of our atomic orbitals which depends explicitly on the magnetic field by Eq. (7) together with Eq. (2), we are now left with the determination of Φ in Eq. (7).

A frequently approved set of atomic orbitals for the calculation of electronic spectra and wave functions in the zero-field case is the spherical Cartesian Gaussian basis

$$x^{n_x}y^{n_y}z^{n_z}\exp(-\alpha \mathbf{r}^2) \tag{9}$$

with $\mathbf{r}^T=(x,y,z)$ and where α is a variational parameter and n_x,n_y,n_z are non-negative integers. In the presence of a strong magnetic field the spherical symmetry of the exponent of the set (9) provides an insufficient description of the wave function. If one takes, for example, for a hydrogen atom the magnetic field direction parallel to the z axis, then in the limit $|\mathbf{B}|\to\infty$ the wave function in the x,y plane becomes a pure two-dimensional isotropic harmonic-oscillator function. This cannot be reproduced by the exponent of the set (9), i.e., one has to choose different variational parameters for the x^2,y^2,z^2 components of the exponent. For an arbitrary direction of the magnetic field also the mixed terms of the kind xy, xz, and yz may be needed. For the atoms mixed terms can be discarded, but for a diatomic molecule in an arbitrary oriented magnetic field, for instance, these mixed terms are indispensible. Here the nuclear axis and the magnetic field axis provide two distinct axes. This leads us to the following choice of Φ:

$$\Phi(\mathbf{r})=x^{n_x}y^{n_y}z^{n_z}\exp(-\alpha_{xx}x^2-\alpha_{yy}y^2-\alpha_{zz}z^2 -2\alpha_{xy}xy-2\alpha_{xz}xz-2\alpha_{yz}yz)\ , \tag{10}$$

with variational parameters $\alpha_{xx},\alpha_{yy},\alpha_{zz},\alpha_{xy},\alpha_{xz},\alpha_{yz}$. For convenience we write the quadratic form of the exponent of Eq. (10) in matrix representation and obtain (atomic units are used throughout)

$$\begin{aligned}\Psi_{\mathrm{n}}&(\mathbf{r};\underline{\alpha},\mathbf{R},\mathbf{C})\\ &=\exp[-i\,\mathbf{A}(\mathbf{C})\mathbf{r}](x-R_x)^{n_x}(y-R_y)^{n_y}(z-R_z)^{n_z}\\ &\quad\times\exp[-(\mathbf{r}-\mathbf{R})^T\underline{\alpha}(\mathbf{r}-\mathbf{R})]\ ,\end{aligned} \tag{11}$$

where the triad $\mathbf{n}^T=(n_x,n_y,n_z)$ is used as an index. $\underline{\alpha}$ is a real symmetric matrix of variational parameters

$$\underline{\alpha}=\begin{bmatrix}\alpha_{xx} & \alpha_{xy} & \alpha_{xz}\\ \alpha_{xy} & \alpha_{yy} & \alpha_{yz}\\ \alpha_{xz} & \alpha_{yz} & \alpha_{zz}\end{bmatrix}\ . \tag{12}$$

The elements of the matrix $\underline{\alpha}$ are *a priori* arbitrary within the normalization conditions on Ψ_{n}. In the case of a diatomic molecule and arbitrary direction of the magnetic field $\mathbf{B}$, two of three off-diagonal parameters of $\underline{\alpha}$ can be taken to be zero by a special choice of the coordinate system.

To facilitate somewhat the choice of atomic orbitals, we present in Table I the ground-state energy of the hydrogen atom obtained by different trial functions. Three different trial functions have been used: (1) a Slater-type function $\exp(-\beta|\mathbf{r}|)$; (2) a single 1*s* Cartesian Gaussian-type function $\exp(-\alpha\mathbf{r}^2)$; (3) a single function of the form (10) with $n_x=n_y=n_z=0$, i.e., $\exp(-\mathbf{r}^T\underline{\alpha}\mathbf{r})$. The quantities α,β and the elements of the matrix $\underline{\alpha}$ are variational parameters which have to be determined for each magnetic field strength $\mathbf{B}$. For weak magnetic fields the Slater-type orbital is in excellent agreement with the best available variational results.[13,14] For $|\mathbf{B}|\geq 1$ a.u. the spherical Gaussian orbital gradually improves and for $|\mathbf{B}|\geq 2$ a.u. becomes superior to the Slater-type orbital. For $|\mathbf{B}|\geq 5$ a.u. the Slater-type and spherical Gaussian-type orbitals are not able to describe the distorted wave functions anymore, whereas our wave function (10) for $n_x=n_y=n_z=0$ is valid over the whole range of magnetic field strengths.

It is clear that for excited states, where even weak fields produce remarkable effects, the number of basis functions out of the set (9) needed for getting accurate results would be very large and, therefore, the calculation no more practicable. In contrast to this the set of atomic orbitals (10) should provide accurate results also for excited states within a "reasonable" number of basis functions. We remark that for every field strength the set (10) is better adapted to the molecular problem than

TABLE I. Ground-state energy of the hydrogen atom for different trial functions and arbitrary directions of $\mathbf{B}$. The energy and magnetic field strength are given in atomic units, i.e., $B=\hbar\omega/R$, where R is the Rydberg energy and ω is half of the cyclotron frequency; $B=1$ a.u. corresponds to $B=2.35\times10^9$ G. α, β, and the elements of the matrix $\underline{\alpha}$ are variational parameters. (Negative energies mean an unbound state.)

Magnetic field strength B (a.u.)	Trial functions $\exp(-\beta\vert\mathbf{r}\vert)$	 $\exp(-\alpha\mathbf{r}^2)$	 $\exp(-\mathbf{r}^T\underline{\alpha}\mathbf{r})$	Best available variational energies (a.u.) (Refs. 13 and 14)
0.0	0.500	0.424	0.424	0.500
0.1	0.548	0.472	0.472	0.547
1.0	0.809	0.757	0.762	0.831
2.0	0.933	0.928	0.953	1.022
5.0	0.989	1.17	1.31	1.380
10.0	0.726	1.27	1.66	1.747
100.0	−12.2	−3.97	3.57	3.786

the set (9), because the function with $n_x = n_y = n_z = 0$ from (10) contains higher-order functions of the type (9) and is able to reproduce a cylindrical symmetry. The basis set defined by (10) and investigated here could be useful for computations on molecules even in the absence of a magnetic field.

III. THE MATRIX ELEMENTS OF THE HAMILTONIAN

In the *zero-field case* and for the choice $\underline{\alpha} = \alpha \underline{1}$, where $\underline{1}$ is the unit matrix, Eq. (11) reduces to the ordinary spherical Cartesian Gaussian atomic orbitals. The matrix elements of the Hamiltonian in this basis set are well known analytically.[38] The matrix elements calculated with a Cartesian Gaussian basis set extended to different exponential coefficients for x^2, y^2, z^2 were presented extensively in the literature.[39] They were used for developing Slater-type orbitals in a series of Gaussians. For the case of a general quadratic form in the exponent the matrix elements of the $\mathbf{n} = 0$ function in the zero-field case were calculated in Ref. 40. In the following we will present the integration of the matrix elements of our basis (11) for general $\mathbf{n}$ and including the position-dependent phase factor due to the vector potential. It should be noted that the basis function (11) is complex in the finite-field case. Before explaining the method of integration we describe the different terms of the Hamiltonian (1) more explicitly. Separating the Hamiltonian into field-independent and field-dependent terms one obtains

$$
\begin{aligned}
H = & -\tfrac{1}{2}\sum_i \nabla_i^2 - \sum_{i,k} \frac{1}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{\substack{i,j \\ i>j}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\
& + \sum_{\substack{k,l \\ k>l}} \frac{1}{|\mathbf{R}_k - \mathbf{R}_l|} + \frac{1}{2i} \sum_i [\nabla_i, \mathbf{A}(\mathbf{r}_i)] \\
& + \frac{1}{i} \sum_i \mathbf{A}(\mathbf{r}_i)\nabla_i + \tfrac{1}{2} \sum_i \mathbf{A}^2(\mathbf{r}_i) , \qquad (13)
\end{aligned}
$$

where the bracket is the commutator. The first four terms are the kinetic energy, electron-nucleus attraction, electron-electron repulsion, and nucleus-nucleus repulsion, respectively. The following two terms give the paramagnetic energy and the last one the diamagnetic contribution. For the mixed gauge (2) of our case, the commutator vanishes.

Before going into technical details of the integration of the individual matrix elements we present a simple formula

$$
\int_{-\infty}^{+\infty} \prod_{i=1}^{3n} dx_i \exp(-\mathbf{x}^T \underline{A} \mathbf{x} + \mathbf{b}^T \mathbf{x}) = \frac{\pi^{3n/2}}{(\det \underline{A})^{1/2}} \exp(+\tfrac{1}{4} \mathbf{b}^T \underline{A}^{-1} \mathbf{b}) , \qquad (14)
$$

where $\underline{A}$ is a real, symmetric, nonsingular matrix and $\mathbf{b}$ is an arbitrary $3n$-dimensional complex column vector. The identity (14) will be helpful in the construction of the matrix elements.

A. Overlap integrals

The overlap integrals to be evaluated are of the form

$$
I_{\mathrm{ov}}(\mathbf{n}_1, \underline{\alpha}_1, \mathbf{R}_1, \mathbf{C}_1; \mathbf{n}_2, \underline{\alpha}_2, \mathbf{R}_2, \mathbf{C}_2) = \int \Psi^*_{\mathbf{n}_1}(\mathbf{r}; \underline{\alpha}_1, \mathbf{R}_1, \mathbf{C}_1) \Psi_{\mathbf{n}_2}(\mathbf{r}; \underline{\alpha}_2, \mathbf{R}_2, \mathbf{C}_2) d\mathbf{r} , \qquad (15)
$$

where the atomic orbitals $\Psi_{\mathbf{n}}(\mathbf{r}; \underline{\alpha}, \mathbf{R}, \mathbf{C})$ are defined in Eq. (11). These overlap integrals can be determined starting from

$$
\begin{aligned}
I_{\mathrm{ov}}(0, \underline{\alpha}_1, \mathbf{R}_1, \mathbf{C}_1; 0, \underline{\alpha}_2, \mathbf{R}_2, \mathbf{C}_2)_{\mathbf{J}} = & \int \Psi^*_0(\mathbf{r}; \underline{\alpha}_1, \mathbf{R}_1, \mathbf{C}_1) \Psi_0(\mathbf{r}; \underline{\alpha}_2, \mathbf{R}_2, \mathbf{C}_2) \\
& \times \exp[+\mathbf{J}^T(\mathbf{r} - \mathbf{R}_1)] d\mathbf{r} . \qquad (16)
\end{aligned}
$$

From Eq. (16) one obtains the general overlap (15) by multiple differentiation with respect to the components of $\mathbf{J}$ and finally setting $\mathbf{J}$ equal to zero,

$$
\begin{aligned}
& I_{\mathrm{ov}}(\mathbf{n}_1, \underline{\alpha}_1, \mathbf{R}_1, \mathbf{C}_1; \mathbf{n}_2, \underline{\alpha}_2, \mathbf{R}_2, \mathbf{C}_2) \\
& = \left[\frac{\partial}{\partial J_x}\right]^{n_{1x}} \left[\frac{\partial}{\partial J_y}\right]^{n_{1y}} \left[\frac{\partial}{\partial J_z}\right]^{n_{1z}} \left[\frac{\partial}{\partial J_x} + (\mathbf{R}_1 - \mathbf{R}_2)_x\right]^{n_{2x}} \left[\frac{\partial}{\partial J_y} + (\mathbf{R}_1 - \mathbf{R}_2)_y\right]^{n_{2y}} \\
& \quad \times \left[\frac{\partial}{\partial J_z} + (\mathbf{R}_1 - \mathbf{R}_2)_z\right]^{n_{2z}} I_{\mathrm{ov}}(0, \underline{\alpha}_1, \mathbf{R}_1, \mathbf{C}_1; 0, \underline{\alpha}_2, \mathbf{R}_2, \mathbf{C}_2)_{\mathbf{J}} \Big|_{\mathbf{J}=0} . \qquad (17)
\end{aligned}
$$

In Eq. (16) one could have chosen two external sources $\mathbf{J}_1$ and $\mathbf{J}_2$ and the terms $\mathbf{J}_1^T(\mathbf{r} - \mathbf{R}_1) + \mathbf{J}_2^T(\mathbf{r} - \mathbf{R}_2)$ instead of $\mathbf{J}^T(\mathbf{r} - \mathbf{R}_1)$ in the exponential. The differential operator in Eq. (17) would then simplify to

$$
\left[\frac{\partial}{\partial J_{1x}}\right]^{n_{1x}} \left[\frac{\partial}{\partial J_{1y}}\right]^{n_{1y}} \left[\frac{\partial}{\partial J_{1z}}\right]^{n_{1z}} \left[\frac{\partial}{\partial J_{2x}}\right]^{n_{2x}} \left[\frac{\partial}{\partial J_{2y}}\right]^{n_{2y}} \left[\frac{\partial}{\partial J_{2z}}\right]^{n_{2z}} .
$$

However, the overlap (16) with $\mathbf{J}_1$ and $\mathbf{J}_2$ would be more complicated to differentiate and therefore we prefer to take only one external source.

The calculation of the overlap (16) is easily performed by combining the quadratic forms of the two wave functions in Eq. (16) and the use of formula (14). The result has the following structure:

$$I_{\mathrm{ov}}(\mathbf{0},\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{0},\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)_{\mathbf{J}}=\pi^{3/2}(\det\underline{\alpha})^{-1/2}\exp(-2\mathbf{R}_1^T\underline{\alpha}_1\mathbf{R}_1-\mathbf{R}_2^T\underline{\alpha}_2\mathbf{R}_2)$$
$$\times\exp[+(\Delta\mathbf{A}+2\mathbf{R})^T\mathbf{R}_1+\tfrac{1}{4}(\Delta\mathbf{A}+\mathbf{J}+2\mathbf{R}-2\underline{\alpha}\mathbf{R}_1)^T\underline{\alpha}^{-1}(\Delta\mathbf{A}+\mathbf{J}+2\mathbf{R}-2\underline{\alpha}\mathbf{R}_1)]\ , \tag{18a}$$

where

$$\underline{\alpha}=\underline{\alpha}_1+\underline{\alpha}_2\ ,$$
$$\mathbf{R}=\underline{\alpha}_1\mathbf{R}_1+\underline{\alpha}_2\mathbf{R}_2\ , \tag{18b}$$
$$\Delta\mathbf{A}=+i[\mathbf{A}(\mathbf{C}_1)-\mathbf{A}(\mathbf{C}_2)]\ .$$

The general form of the overlap (15) can be obtained by substituting Eq. (18a) into Eq. (17) and performing the differentiations. It takes on the following appearance:

$$I_{\mathrm{ov}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)=I_{\mathrm{ov}}(\mathbf{0},\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{0},\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)\mathcal{F}(\mathbf{n}_1,\mathbf{n}_2;\mathbf{R}_1-\mathbf{R}_2;\Delta\mathbf{A}+2\mathbf{R}-2\underline{\alpha}\mathbf{R}_1;\underline{\alpha}^{-1})\ . \tag{19}$$

We note that the function $\mathcal{F}$ has the symmetry property

$$\mathcal{F}(\mathbf{n}_1,\mathbf{n}_2;\mathbf{R}_1-\mathbf{R}_2;\Delta\mathbf{A}+2\mathbf{R}-2\underline{\alpha}\mathbf{R}_1;\underline{\alpha}^{-1})=\mathcal{F}(\mathbf{n}_2,\mathbf{n}_1;\mathbf{R}_2-\mathbf{R}_1;\Delta\mathbf{A}+2\mathbf{R}-2\underline{\alpha}\mathbf{R}_2;\underline{\alpha}^{-1})\ , \tag{20}$$

which arises from the fact that neither of the two centers $\mathbf{R}_1$ and $\mathbf{R}_2$ is distinct. $\mathcal{F}$ can be generated by the equation

$$\mathcal{F}(\mathbf{n}_1,\mathbf{n}_2;\mathbf{R}_1-\mathbf{R}_2;\mathbf{b};\underline{A})=\sum_{\nu_x=0}^{n_{2x}}\sum_{\nu_y=0}^{n_{2y}}\sum_{\nu_z=0}^{n_{2z}}\begin{bmatrix}n_{2x}\\ \nu_x\end{bmatrix}\begin{bmatrix}n_{2y}\\ \nu_y\end{bmatrix}\begin{bmatrix}n_{2z}\\ \nu_z\end{bmatrix}(\mathbf{R}_1-\mathbf{R}_2)_x^{n_{2x}-\nu_x}$$
$$\times(\mathbf{R}_1-\mathbf{R}_2)_y^{n_{2y}-\nu_y}(\mathbf{R}_1-\mathbf{R}_2)_z^{n_{2z}-\nu_z}Q_{\mathcal{F}}(\boldsymbol{\nu}+\mathbf{n}_1;\mathbf{b};\underline{A}) \tag{21}$$

with the notation $\boldsymbol{\nu}^T=(\nu_x,\nu_y,\nu_z)$, $\mathbf{n}_1^T=(n_{1x},n_{1y},n_{1z})$. $\mathbf{b}$ and $\underline{A}$ are an arbitrary column vector and a real symmetric matrix, respectively. The function $Q_{\mathcal{F}}$ is given by

$$Q_{\mathcal{F}}(\boldsymbol{\nu};\mathbf{b};\underline{A})=\exp(-\tfrac{1}{4}\mathbf{b}^T\underline{A}\mathbf{b})\left[\frac{\partial}{\partial b_x}\right]^{\nu_x}\left[\frac{\partial}{\partial b_y}\right]^{\nu_y}\left[\frac{\partial}{\partial b_z}\right]^{\nu_z}\exp(+\tfrac{1}{4}\mathbf{b}^T\underline{A}\mathbf{b})\ . \tag{22}$$

The explicit form of the function $Q_{\mathcal{F}}$, which is a polynomial in the components of the vector $\mathbf{b}$ and the matrix $\underline{A}$, is given in the Appendix. As can be seen from Eq. (22) $Q_{\mathcal{F}}$ can be considered as a generalization of the Hermite polynomials to several dimensions.

Another possibility to calculate the function $Q_{\mathcal{F}}$, i.e., the general overlap, would be to diagonalize the real symmetric matrix $\underline{A}$ in Eq. (22) by an orthogonal transformation. Although the exponential function in this case is a simple product of generators of Hermite polynomials in three dimensions, the calculation is by no means easier, because one has to transform the derivatives with respect to $\mathbf{b}$ with the same orthogonal transformation. It is left to the reader which method he prefers to generate $\mathcal{F}$. Finally, we remark that for atomic orbitals with not too high polynomial exponents, it is more convenient to use Eq. (22) than the explicit expression for $Q_{\mathcal{F}}$ in the Appendix.

B. Kinetic energy

The matrix elements of the kinetic energy as well as of the paramagnetic and diamagnetic terms can be expressed as a linear combination of overlaps. The general matrix element for the kinetic energy has the form

$$E_K(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)=(-\tfrac{1}{2})\int\Psi_{\mathbf{n}_1}^*(\mathbf{r};\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1)\nabla^2\Psi_{\mathbf{n}_2}(\mathbf{r};\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)d\mathbf{r}\ . \tag{23}$$

The result of the differentiation is written as a linear combination of polynomials with different exponents, i.e., as a linear combination of overlaps

$$E_K(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)$$
$$=(-\tfrac{1}{2})\Bigg[I_{\mathrm{ov}}(\mathbf{0})[-2\,\mathrm{Tr}(\underline{\alpha}_2)-\mathbf{A}^2(\mathbf{C}_2)]+2\sum_{k=1}^{3}I_{\mathrm{ov}}(-\mathbf{e}_k)(\mathbf{n}_2)_k[-i\,\mathbf{A}(\mathbf{C}_2)]_k$$
$$+\sum_{k=1}^{3}I_{\mathrm{ov}}(-2\mathbf{e}_k)(\mathbf{n}_2)_k(\mathbf{n}_2-\mathbf{1})_k+4\sum_{k=1}^{3}I_{\mathrm{ov}}(\mathbf{e}_k)\{[i\,\mathbf{A}(\mathbf{C}_2)]^T[\underline{\alpha}_2)]\}_k$$
$$-4\sum_{i,j=1}^{3}I_{\mathrm{ov}}(\mathbf{e}_i-\mathbf{e}_j)\{[\mathbf{n}_2]_j[\underline{\alpha}_2]_{ji}\}+4\sum_{i,j=1}^{3}I_{\mathrm{ov}}(\mathbf{e}_i+\mathbf{e}_j)(\underline{\alpha}_2^2)_{ij}\Bigg]\ , \tag{24}$$

where $\mathbf{1}^T=(1,1,1)$ and Tr means the trace. $\{\mathbf{e}_i\}$ are the unit axis vectors of the orthogonal Cartesian coordinate system. Furthermore, we have used the abbreviation

$$I_{\text{ov}}(\mathbf{v})=I_{\text{ov}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2+\mathbf{v},\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)\ . \tag{25}$$

In Secs. III C and III D we give the results for the matrix elements which involve the magnetic field.

C. Paramagnetic energy integrals

The matrix elements, arising from the term linear in the magnetic field of the Hamiltonian (13), can all be obtained by linear combination of matrix elements of the following type [for convenience we use $\mathbf{r}^T=(x_1,x_2,x_3)$]:

$$I_{\text{PM}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)_{ij}=\int \Psi^*_{\mathbf{n}_1}(\mathbf{r};\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1)x_i\frac{\partial}{\partial x_j}\Psi_{\mathbf{n}_2}(\mathbf{r};\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)d\mathbf{r}\ , \tag{26}$$

where $i\neq j$. The result, written in terms of overlaps, is

$$\begin{aligned}I_{\text{PM}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)_{ij}=\{&(\mathbf{n}_2)_j[I_{\text{ov}}(\mathbf{e}_i-\mathbf{e}_j)+(\mathbf{R}_2)_iI_{\text{ov}}(-\mathbf{e}_j)]-2(\underline{\alpha}_2)_{jj}[I_{\text{ov}}(\mathbf{e}_i+\mathbf{e}_j)+(\mathbf{R}_2)_iI_{\text{ov}}(\mathbf{e}_j)]\\&+[-i\,\mathbf{A}(\mathbf{C}_2)]_j[I_{\text{ov}}(\mathbf{e}_i)+(\mathbf{R}_2)_iI_{\text{ov}}(\mathbf{0})]-2(\underline{\alpha}_2)_{ij}[I_{\text{ov}}(2\mathbf{e}_i)+(\mathbf{R}_2)_iI_{\text{ov}}(\mathbf{e}_i)]\\&-2(\underline{\alpha}_2)_{kj}[I_{\text{ov}}(\mathbf{e}_i+\mathbf{e}_k)+(\mathbf{R}_2)_iI_{\text{ov}}(\mathbf{e}_k)]\}\end{aligned} \tag{27}$$

with the notation of Eq. (25) and where (i,j,k) is out of the permutations of the numbers in the triad (1,2,3). In the case of the symmetric gauge the paramagnetic terms can be expressed by the components of the angular momentum, whose matrix elements can be obtained from Eq. (27) through antisymmetric linear combination.

D. Diamagnetic energy integrals

The matrix elements of the diamagnetic term of the Hamiltonian (13) are the most easiest to evaluate. They have the following form:

$$\begin{aligned}&I_{\text{DM}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)_{ij}\\&\quad=\int \Psi^*_{\mathbf{n}_1}(\mathbf{r};\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1)x_ix_j\Psi_{\mathbf{n}_2}(\mathbf{r};\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)d\mathbf{r}\end{aligned} \tag{28}$$

and the result in terms of overlaps is

$$\begin{aligned}&I_{\text{DM}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)_{ij}\\&\quad=\sum_{\mu=0}^{1}\sum_{\nu=0}^{1}I_{\text{ov}}(\mu\mathbf{e}_i+\nu\mathbf{e}_j)(\mathbf{R}_2)_i^{1-\mu}(\mathbf{R}_2)_j^{1-\nu}\ .\end{aligned} \tag{29}$$

In Secs. III E and III F we calculate the electron-nucleus and electron-electron matrix elements.

E. Electron-nucleus attraction integrals

The general three-center integral to be evaluated has the form

$$\begin{aligned}&I_{\text{NA}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{R}_3;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)\\&\quad=\int \Psi^*_{\mathbf{n}_1}(\mathbf{r};\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1)\frac{1}{|\mathbf{r}-\mathbf{R}_3|}\Psi_{\mathbf{n}_2}(\mathbf{r};\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)d\mathbf{r}\ .\end{aligned} \tag{30}$$

To evaluate this type of integral we follow Singer[40] and use the transformation

$$\begin{aligned}\frac{1}{f(\mathbf{r})}&=\pi^{-1/2}\int_{-\infty}^{+\infty}\exp[-u^2f^2(\mathbf{r})]du\\&=\frac{2}{\pi^{1/2}}\int_0^1\exp\left[-f^2(\mathbf{r})\frac{v^2}{1-v^2}\right]\frac{dv}{(1-v^2)^{3/2}}\ .\end{aligned} \tag{31}$$

In our case we have $f(\mathbf{r})=|\mathbf{r}-\mathbf{R}_3|$. The second integration in Eq. (31) can be performed more easily, because of the compact integration interval. The introduction of the additional integration enables us to perform the three space integrations. The basic matrix element to be evaluated is then

$$\begin{aligned}I_{\text{NA}}(\mathbf{0},\underline{\alpha}_1\mathbf{R}_1,\mathbf{C}_1;\mathbf{R}_3;\mathbf{0},\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)_{\mathbf{J}}=\frac{2}{\pi^{1/2}}\int\int_0^1&\Psi^*_0(\mathbf{r};\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1)\exp\left[-[\mathbf{r}-\mathbf{R}_3]^2\frac{v^2}{(1-v^2)}\right]\Psi_0(\mathbf{r};\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)\\&\times\exp(+\mathbf{J}^T[\mathbf{r}-\mathbf{R}_1])\frac{dv}{(1-v^2)^{3/2}}d\mathbf{r}\ .\end{aligned} \tag{32}$$

From Eq. (32) one obtains the general form (30) in analogy to Eq. (17) by differentiation with respect to the components of **J**.

The calculation of the matrix element (32) is performed analogously to the overlap integration in Eq. (16). One just combines the three quadratic forms and uses formula (14). The result reads

$$I_{\mathrm{NA}}(\mathbf{0},\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{R}_3;\mathbf{0},\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)_{\mathbf{J}}=T_1\int_0^1 T_2(v)dv \tag{33a}$$

with

$$T_1=2\pi\exp(-\mathbf{R}_1^T\underline{\alpha}_1\mathbf{R}_1-\mathbf{R}_2^T\underline{\alpha}_2\mathbf{R}_2+\Delta\mathbf{A}^T\mathbf{R}_1)\ , \tag{33b}$$

$$\begin{aligned}T_2=&(\det\underline{\alpha}_v)^{-1/2}(1-v^2)^{-3/2}\\&\times\exp(-\mathbf{R}_3^T\underline{\hat{v}}\mathbf{R}_3-\mathbf{R}_1^T\underline{\alpha}_v\mathbf{R}_1+2\mathbf{R}_v^T\mathbf{R}_1)\\&\times\exp[+\tfrac{1}{4}(\Delta\mathbf{A}+\mathbf{J}+2\mathbf{R}_v-2\underline{\alpha}_v\mathbf{R}_1)^T\\&\qquad\times\underline{\alpha}_v^{-1}(\Delta\mathbf{A}+\mathbf{J}+2\mathbf{R}_v-2\underline{\alpha}_v\mathbf{R}_1)]\ ,\end{aligned}$$

and the abbreviations

$$\begin{aligned}&\underline{\hat{v}}=\left[\frac{v^2}{1-v^2}\right]\times\underline{1}\ ,\\&\underline{\alpha}_v=\underline{\alpha}_1+\underline{\alpha}_2+\underline{\hat{v}}\ ,\\&\mathbf{R}_v=\underline{\alpha}_1\mathbf{R}_1+\underline{\alpha}_2\mathbf{R}_2+\underline{\hat{v}}\mathbf{R}_3\ .\end{aligned} \tag{33c}$$

From this form one obtains in analogy to Eq. (19) the general matrix element (30)

$$\begin{aligned}I_{\mathrm{NA}}&(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{R}_3;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)\\&=T_1\int_0^1 T_2(v)\,|_{\mathbf{J}=0}\mathcal{J}(\mathbf{n}_1,\mathbf{n}_2;\mathbf{R}_1-\mathbf{R}_2;\Delta\mathbf{A}\\&\qquad+2\mathbf{R}_v-2\underline{\alpha}_v\mathbf{R}_1;\underline{\alpha}_v^{-1})dv\ ,\end{aligned} \tag{34}$$

where $\mathcal{J}$ was already discussed in Sec. III A in connection with the overlap integrals. The remaining single integration must be performed numerically. This causes no problems because the integrand is smooth and the numerical integration converges very fast.

F. Interelectronic potential energy integrals

This type of matrix element involves at most four centers $\{\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3,\mathbf{R}_4\}$. The general matrix element is given by

$$\begin{aligned}I_{\mathrm{EE}}&(\mathbf{0},\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{0},\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2;\mathbf{0},\underline{\alpha}_3,\mathbf{R}_3,\mathbf{C}_3;\mathbf{0},\underline{\alpha}_4,\mathbf{R}_4,\mathbf{C}_4)_{\mathbf{J}}\\&=\int\Psi_{\mathbf{n}_1}^*(\mathbf{r}_1;\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1)\Psi_{\mathbf{n}_2}^*(\mathbf{r}_2;\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\Psi_{\mathbf{n}_3}(\mathbf{r}_1;\underline{\alpha}_3,\mathbf{R}_3,\mathbf{C}_3)\Psi_{\mathbf{n}_4}(\mathbf{r}_2;\underline{\alpha}_4,\mathbf{R}_4,\mathbf{C}_4)d\mathbf{r}_1d\mathbf{r}_2\ .\end{aligned} \tag{35}$$

We introduce two external sources $\mathbf{J}_1$ and $\mathbf{J}_2$ for the two electrons and use transformation (31), thus arriving at the basic integral

$$\begin{aligned}I_{\mathrm{EE}}&(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2;\mathbf{n}_3,\underline{\alpha}_3,\mathbf{R}_3,\mathbf{C}_3;\mathbf{n}_4,\underline{\alpha}_4,\mathbf{R}_4,\mathbf{C}_4)\\&=\frac{2}{\pi^{1/2}}\int\int_0^1\Psi_0^*(\mathbf{r}_1;\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1)\Psi_0^*(\mathbf{r}_2;\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2)\exp\left[-(\mathbf{r}_1-\mathbf{r}_2)^2\frac{v^2}{1-v^2}\right]\\&\qquad\times\Psi_0(\mathbf{r}_1;\underline{\alpha}_3,\mathbf{R}_3,\mathbf{C}_3)\Psi_0(\mathbf{r}_2;\underline{\alpha}_4,\mathbf{R}_4,\mathbf{C}_4)\exp(+\mathbf{J}_1^T[\mathbf{r}_1-\mathbf{R}_1]+\mathbf{J}_2^T[\mathbf{r}_2-\mathbf{R}_2])\frac{dv}{(1-v^2)^{3/2}}d\mathbf{r}_1d\mathbf{r}_2\ .\end{aligned} \tag{36}$$

To evaluate the integral (36) it is useful to go to a six-dimensional representation. The new variables now read

$$\begin{aligned}&\underline{\alpha}_{12}=\begin{bmatrix}\underline{\alpha}_1 & 0\\ 0 & \underline{\alpha}_2\end{bmatrix}\ ,\\&\underline{\alpha}_{34}=\begin{bmatrix}\underline{\alpha}_3 & 0\\ 0 & \underline{\alpha}_4\end{bmatrix}\ ,\\&\Delta\mathbf{A}=i\begin{bmatrix}\mathbf{A}(\mathbf{C}_1)-\mathbf{A}(\mathbf{C}_3)\\ \mathbf{A}(\mathbf{C}_2)-\mathbf{A}(\mathbf{C}_4)\end{bmatrix}\ ,\\&\mathbf{r}=\begin{bmatrix}\mathbf{r}_1\\ \mathbf{r}_2\end{bmatrix},\quad\mathbf{R}_{12}=\begin{bmatrix}\mathbf{R}_1\\ \mathbf{R}_2\end{bmatrix},\quad\mathbf{R}_{34}=\begin{bmatrix}\mathbf{R}_3\\ \mathbf{R}_4\end{bmatrix},\quad\mathbf{J}=\begin{bmatrix}\mathbf{J}_1\\ \mathbf{J}_2\end{bmatrix}\ ,\\&\tilde{\underline{1}}=\begin{bmatrix}\underline{1} & -\underline{1}\\ -\underline{1} & \underline{1}\end{bmatrix},\quad\hat{v}=\frac{v^2}{1-v^2}\ .\end{aligned} \tag{37}$$

Rewriting the integral (36) in these variables, we arrive at

$$I_{\mathrm{EE}}(0,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;0,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2;0,\underline{\alpha}_3,\mathbf{R}_3,\mathbf{C}_3;0,\underline{\alpha}_4,\mathbf{R}_4,\mathbf{C}_4)_{\mathbf{J}}$$

$$=\frac{2}{\pi^{1/2}}\int\int_0^1 \exp(+\Delta\,\mathbf{A}^T\mathbf{r})\exp(-[\mathbf{r}-\mathbf{R}_{12}]^T\underline{\alpha}_{12}[\mathbf{r}-\mathbf{R}_{12}]-[\mathbf{r}-\mathbf{R}_{34}]^T\underline{\alpha}_{34}[\mathbf{r}-\mathbf{R}_{34}]-\mathbf{r}^T\hat{v}\,\tilde{\underline{1}}\mathbf{r})$$

$$\times\exp(+\mathbf{J}^T[\mathbf{r}-\mathbf{R}_{12}])\frac{dv}{(1-v^2)^{3/2}}d\mathbf{r}\ . \tag{38}$$

Combining the three quadratic forms with the matrices $\underline{\alpha}_{12},\underline{\alpha}_{34},\hat{v}\,\tilde{\underline{1}}$ and using formula (14) gives the following final result for the basic function which contains a single integration only:

$$I_{\mathrm{EE}}(0,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;0,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2;0,\underline{\alpha}_3,\mathbf{R}_3,\mathbf{C}_3;0,\underline{\alpha}_4,\mathbf{R}_4,\mathbf{C}_4)_{\mathbf{J}}=T_3\int_0^1 T_4(v)dv \tag{39a}$$

with

$$T_3=2\pi^{5/2}\exp(-\mathbf{R}_{12}^T\underline{\alpha}_{12}\mathbf{R}_{12}-\mathbf{R}_{34}^T\underline{\alpha}_{34}\mathbf{R}_{34}+\mathbf{R}_{12}^T[\Delta\,\mathbf{A}+2\mathbf{R}])\ ,$$

$$T_4=(\det\underline{\alpha}_v)^{-1/2}(1-v^2)^{-3/2}\exp(-\mathbf{R}_{12}^T\underline{\alpha}_v\mathbf{R}_{12})\exp(+\tfrac{1}{4}[\Delta\,\mathbf{A}+\mathbf{J}+2\mathbf{R}-2\underline{\alpha}_v\mathbf{R}_{12}]^T\underline{\alpha}_v^{-1}[\Delta\,\mathbf{A}+\mathbf{J}+2\mathbf{R}-2\underline{\alpha}_v\mathbf{R}_{12}])\ , \tag{39b}$$

and the notation

$$\underline{\alpha}_v=\underline{\alpha}_{12}+\underline{\alpha}_{34}+\hat{v}\,\tilde{\underline{1}}\ ,$$

$$\mathbf{R}=\underline{\alpha}_{12}\mathbf{R}_{12}+\underline{\alpha}_{34}\mathbf{R}_{34}\ . \tag{39c}$$

The general matrix element (35) again is obtained from the matrix element (39a) by differentiation with respect to the components of $\mathbf{J}$. It takes on the following appearance:

$$I_{\mathrm{EE}}(\mathbf{n}_1,\underline{\alpha}_1,\mathbf{R}_1,\mathbf{C}_1;\mathbf{n}_2,\underline{\alpha}_2,\mathbf{R}_2,\mathbf{C}_2;\mathbf{n}_3,\underline{\alpha}_3,\mathbf{R}_3,\mathbf{C}_3;\mathbf{n}_4,\underline{\alpha}_4,\mathbf{R}_4,\mathbf{C}_4)$$

$$=T_3\int_0^1 T_4(v)\,|_{\mathbf{J}=0}\mathcal{H}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{n}_3,\mathbf{n}_4;\mathbf{R}_1-\mathbf{R}_3,\mathbf{R}_2-\mathbf{R}_4;\Delta\,\mathbf{A}+2\mathbf{R}-2\underline{\alpha}_v\mathbf{R}_{12};\underline{\alpha}_v^{-1})dv\ . \tag{40}$$

In analogy to Eq. (20) there exists a symmetry of $\mathcal{H}$,

$$\mathcal{H}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{n}_3,\mathbf{n}_4;\mathbf{R}_1-\mathbf{R}_3,\mathbf{R}_2-\mathbf{R}_4;\Delta\,\mathbf{A}+2\mathbf{R}-2\underline{\alpha}_v\mathbf{R}_{12};\underline{\alpha}_v^{-1})=\mathcal{H}(\mathbf{n}_3,\mathbf{n}_4,\mathbf{n}_1,\mathbf{n}_2;\mathbf{R}_3-\mathbf{R}_1,\mathbf{R}_4-\mathbf{R}_2;\Delta\,\mathbf{A}+2\mathbf{R}-2\underline{\alpha}_v\mathbf{R}_{34};\underline{\alpha}_v^{-1})$$

$$=\mathcal{H}(\mathbf{n}_3,\mathbf{n}_2,\mathbf{n}_1,\mathbf{n}_4;\mathbf{R}_3-\mathbf{R}_1,\mathbf{R}_2-\mathbf{R}_4;\Delta\,\mathbf{A}+2\mathbf{R}-2\underline{\alpha}_v\mathbf{R}_{32};\underline{\alpha}_v^{-1})\ . \tag{41}$$

$\mathcal{H}$ can be generated by the equation

$$\mathcal{H}(\mathbf{n}_1,\mathbf{n}_2,\mathbf{n}_3,\mathbf{n}_4;\mathbf{R}_1-\mathbf{R}_3,\mathbf{R}_2-\mathbf{R}_4;\mathbf{b};\underline{A})$$

$$=\sum_{\mu_1=0}^{n_{3x}}\sum_{\mu_2=0}^{n_{3y}}\sum_{\mu_3=0}^{n_{3z}}\sum_{\mu_4=0}^{n_{4x}}\sum_{\mu_5=0}^{n_{4y}}\sum_{\mu_6=0}^{n_{4z}}\begin{bmatrix}n_{3x}\\ \mu_1\end{bmatrix}\begin{bmatrix}n_{3y}\\ \mu_2\end{bmatrix}\begin{bmatrix}n_{3z}\\ \mu_3\end{bmatrix}\begin{bmatrix}n_{4x}\\ \mu_4\end{bmatrix}\begin{bmatrix}n_{4y}\\ \mu_5\end{bmatrix}\begin{bmatrix}n_{4z}\\ \mu_6\end{bmatrix}$$

$$\times(\mathbf{R}_1-\mathbf{R}_3)_x^{n_{3x}-\mu_1}(\mathbf{R}_1-\mathbf{R}_3)_y^{n_{3y}-\mu_2}(\mathbf{R}_1-\mathbf{R}_3)_z^{n_{3z}-\mu_3}(\mathbf{R}_2-\mathbf{R}_4)_x^{n_{4x}-\mu_4}$$

$$\times(\mathbf{R}_2-\mathbf{R}_4)_y^{n_{4y}-\mu_5}(\mathbf{R}_2-\mathbf{R}_4)_z^{n_{4z}-\mu_6}\times Q_{\mathcal{H}}(\mathbf{n}+\boldsymbol{\mu};\mathbf{b};\underline{A})\ , \tag{42}$$

where the notation $\mathbf{n}^T=(\mathbf{n}_1^T,\mathbf{n}_2^T)$, $\boldsymbol{\mu}^T=(\mu_1,\ldots,\mu_6)$ was used. $\mathbf{b}^T=(\mathbf{b}_1^T,\mathbf{b}_2^T)$ is an arbitrary vector, $\underline{A}$ a symmetric matrix. The function $\mathcal{Q}_{\mathcal{H}}$ is a polynomial in the components of the vector $\mathbf{b}$ and the matrix $\underline{A}$ and given by

$$\mathcal{Q}_{\mathcal{H}}(\boldsymbol{\mu};\mathbf{b};\underline{A})=\exp(-\tfrac{1}{4}\mathbf{b}^T\underline{A}\mathbf{b})\left[\frac{\partial}{\partial b_{1x}}\right]^{\mu_1}\times\cdots\times\left[\frac{\partial}{\partial b_{2z}}\right]^{\mu_6}\times\exp(+\tfrac{1}{4}\mathbf{b}^T\underline{A}\mathbf{b}) \ . \tag{43}$$

The explicit form of $\mathcal{Q}_{\mathcal{H}}$ is given in the Appendix. We remark here only that $\mathcal{Q}_{\mathcal{H}}$ is just the six-dimensional analogue of $\mathcal{Q}_{\mathcal{J}}$.

IV. SUMMARY

We have presented a basis set of atomic orbitals suitable for the calculation of molecular electronic wave functions in a magnetic field of arbitrary strength. This basis set contains the spherical Cartesian Gaussian basis set as a special case and enables one to calculate molecular electronic spectra and wave functions in the usual way from the Hamiltonian matrix elements.

One part of our atomic orbitals is a vector-potential-dependent phase which ensures the correct gauge centering and the correct diamagnetic energies in the dissociation limit. The gauge of the vector potential, occurring in the phase of the atomic orbitals and the Hamiltonian, is the so-called mixed gauge whose parameters are fixed by minimizing the energy. As a consequence the energies calculated with our atomic orbitals should be very near to the gauge-invariant ones, independent of the orientation of the molecule relatively to the magnetic field axis.

The field-independent part of our atomic orbitals is a Cartesian Gaussian function with a general quadratic form in the exponent. This enables us to reproduce any anisotropy, necessary to describe the wave functions of molecules in an arbitrary oriented magnetic field. A calculation of the ground-state energy of the hydrogen atom with only one function of our type shows most promising results over the whole region of magnetic field strengths.

We have evaluated all the matrix elements of the Hamiltonian of a molecule in a magnetic field with our atomic orbitals. Most of them are given analytically, only the electron-nucleus attraction and the electron-electron repulsion still contain a single integration to be performed numerically. This integration converges rapidly.

We note that our atomic orbitals should provide better results also for the zero-field case, as, for instance, the spherical Cartesian Gaussian basis, because it is better adapted to the anisotropy of the molecular wave function. It is now left to future investigations to calculate the electronic and in consequence vibrational properties of molecules with the provided method.

ACKNOWLEDGMENTS

One of the authors (P.S.) acknowledges financial support from Baden-Württemberg (LGFG). We thank H.-D. Meyer for stimulating discussions.

APPENDIX

In the following we present the explicit formulas for the functions $\mathcal{Q}_{\mathcal{J}}$ and $\mathcal{Q}_{\mathcal{H}}$. This explicit form can be obtained by carrying out all possible differentiations, for instance, in Eq. (17). $\mathcal{Q}_{\mathcal{J}}$ and $\mathcal{Q}_{\mathcal{H}}$ are special cases of the general formula

$$\mathcal{Q}_N(\boldsymbol{\mu};\mathbf{b};\underline{A})=\sum_{\rho_1=0}^{\mu_1}\cdots\sum_{\rho_N=0}^{\mu_N}\left[\prod_{i=1}^{N}\binom{\mu_i}{\rho_i}[\tfrac{1}{2}(\underline{A}\mathbf{b})_i]^{\mu_i-\rho_i}\right]\times\sum_{\sum_{l=1}^{N}(1+\delta_{kl})\nu_{kl}=\rho_k}\left\{\left[\prod_{i,j=1}^{N}\frac{\rho_i!}{[(1+\delta_{ij})\nu_{ij}]!}\right]\left[\prod_{i=1}^{N}(\tfrac{1}{2}A_{ii})^{\nu_{ii}}(2\nu_{ii}-1)!\right]\times\left[\prod_{\substack{i,j=1\\ i>j}}^{N}(\tfrac{1}{2}A_{ij})^{\nu_{ij}}(\nu_{ij})!\right]\right\} , \tag{A1}$$

where $\sum_{l=1}^{N}(1+\delta_{kl})\nu_{kl}=\rho_k$, appearing under the summation sign, restricts the summation to run over all $\{\nu_{kl}\}$ which fulfill these N equations $(k=1,\ldots,N)$. δ_{kl} is the Kronecker symbol. The indices ν_{kl} form a symmetric matrix, i.e., $\nu_{kl}=\nu_{lk}$. $\mathbf{b}$ and $\underline{A}$ are an arbitrary column vector and a symmetric matrix in N dimensions. The notations $\mathbf{b}^T=(b_1,\ldots,b_N)$, $\boldsymbol{\mu}^T=(\mu_1,\ldots,\mu_N)$ were used.

$\mathcal{Q}_{\mathcal{J}}$, occurring in the overlap and the electron-nucleus attraction integrals and $\mathcal{Q}_{\mathcal{H}}$, occurring in the electron-electron repulsion integrals, are now simply given by

$$\mathcal{Q}_{\mathcal{J}}(\boldsymbol{\mu};\mathbf{b};\underline{A})=\mathcal{Q}_3(\boldsymbol{\mu};\mathbf{b};\underline{A}) \ ,$$
$$\mathcal{Q}_{\mathcal{H}}(\boldsymbol{\mu};\mathbf{b};\underline{A})=\mathcal{Q}_6(\boldsymbol{\mu};\mathbf{b};\underline{A}) \ . \tag{A2}$$

In the case of $n_x+n_y+n_z\le 2$, i.e., the analogue to the s,p,d functions in the spherical Cartesian Gaussian basis, the expressions for $\mathcal{Q}_{\mathcal{J}}$ and $\mathcal{Q}_{\mathcal{H}}$ in Eq. (A2) reduce to a few terms only.

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