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Study of Reaction Mechanisms by Semiempirical Methods. I.

Optimization of the Geometry of the Molecule in the Framework of a Single Calculation of the Energy Function

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The author suggests a procedure offering the possibility to determine, with the use of a double iteration technique, the equilibrium geometry within the framework of a single calculation of the energy function. The method is used for the ground state and the lowest excited singlet state of formaldehyde and for the formyl radical. The individual contributions of the potential energy are discussed in brief.

Der Autor schlägt ein Verfahren vor, das erlaubt, mittels einer Doppeliterationstechnik die Gleichgewichtsgeometrie im Laufe einer einzigen Berechnung der Energiefunktion zu bestimmen. Das Verfahren wird auf den Grund- und den ersten angeregten Zustand von Formaldehyd und auf das Formylradikal angewendet. Die einzelnen Beiträge zur potentiellen Energie werden kurz diskutiert.

L'auteur propose une méthode par laquelle il est possible de déterminer par une technique iterative double la géometrie d'équilibre dans le cadre d'un seul cálcul de la fonction énergétique. On a appliqué la méthode pour l'état fondamental et l'état excité le plus bas singulet de formaldéhyde et pour HCO. On discute brevement les contributions singulaires de l'énergie potentielle.

Introduction

Semiempirical methods working with all valency electrons [1–5] were successfully employed for determining the equilibrium geometry of molecules [3–7]. The usual procedure in such calculations, i.e., the determination of the shape of the energetic hyper-surface, however, is fairly costly and not feasible for molecules with more than four independent coordinates. The number of the necessary calculations of the energy function was considerably reduced by the procedure of McIver and Komornicki [8], who by means of a quadratically convergent variable metric method minimized the total energy of a molecule obtained with the use of EHT and MINDO/2 programs [1, 5].

In the present paper we have suggested a procedure, which by means of double iteration technique permits the equilibrium geometry in the framework of a single calculation of the energy function to be determined. We have applied this procedure also to the CNDO/2 method [6], of which it is known [9, 10] that it affords a better agreement between the theoretical and the experimental equilibrium geometries than that obtained by the method mentioned earlier. We extended the procedure to the case of excited states (half-electron method [11]) and to radicals (method of Longuet-Higgins and Pople [12]). Although we have tested the procedure on calculations of equilibrium geometries, our main interest is concerned with questions of the reactivity of small molecules and of principal functional groups. To this theme we shall pay our attention in the following papers.

Theoretical Procedure

Among numerical methods used for finding a stationary point of the given function, the most efficient are those which utilize the properties of the gradient [13, 14]. The calculation of the gradient requires a knowledge of the derivative of the overall energy of the molecule with respect to the x-th Cartesian coordinate $n_{x\mathrm{A}}$ of the atom A. For the ground singlet state and the CNDO/2 method we can derive the relation

$$\begin{aligned}\frac{\partial E}{\partial n_{x\mathrm{A}}} &= \sum_{\mathrm{B}\neq\mathrm{A}} \left[Z_{\mathrm{A}} Z_{\mathrm{B}} \frac{\partial R_{\mathrm{AB}}^{-1}}{\partial n_{x\mathrm{A}}} - (P_{\mathrm{AA}} Z_{\mathrm{B}} + P_{\mathrm{BB}} Z_{\mathrm{A}} - P_{\mathrm{AA}} P_{\mathrm{BB}}) \frac{\partial \gamma_{\mathrm{AB}}}{\partial n_{x\mathrm{A}}} \right] \\ &+ \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} \left[2P_{\mu\nu} \frac{\partial \beta_{\mu\nu}}{\partial n_{x\mathrm{A}}} - \frac{1}{2} P_{\mu\nu}^2 \frac{\partial \gamma_{\mathrm{AB}}}{\partial n_{x\mathrm{A}}} \right]\end{aligned} \tag{1}$$

where R_{AB} and γ_{AB} denote the distance and the bicentric repulsion integral between the atoms A and B; Z_{A} and P_{AA} stand for the "core" charge and the electron density on the atom A; $P_{\mu\nu}$ and $\beta_{\mu\nu}$ denote the bond order and the resonance integral between the atomic orbitals μ and ν localized on the atoms A and B. For an open shell system we can use the formula

$$\frac{\partial E}{\partial n_{x\mathrm{A}}} = D - 0.5 \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} c_{m\mu}^2 c_{m\nu}^2 \frac{\partial \gamma_{\mathrm{AB}}}{\partial n_{x\mathrm{A}}} \tag{2}$$

where D is the right hand side of Eq. (1), and $c_{m\mu}$ denotes the expansion coefficient of the μ-th AO in the singly occupied MO (marked with m).

The derivative of the energy change in the excitation of the electron from the level i to j is described by the equation

$$\begin{aligned}\frac{\partial E}{\partial n_{x\mathrm{A}}} = D - 0.5 \sum_{\mathrm{B}\neq\mathrm{A}} \sum_{\mu}^{\mathrm{A}} \sum_{\nu}^{\mathrm{B}} (&c_{i\mu}^2 c_{i\nu}^2 + c_{j\mu}^2 c_{j\nu}^2 \\ &- 2c_{i\mu} c_{j\mu} c_{i\nu} c_{j\nu} \pm 4c_{i\mu} c_{j\mu} c_{i\nu} c_{j\nu}) \frac{\partial \gamma_{\mathrm{AB}}}{\partial n_{x\mathrm{A}}}\end{aligned} \tag{3}$$

where the upper sign holds for a singlet state and the lower for a triplet state. For the INDO method, Eqs. (1)–(3) apply without any change. For the MINDO/2 method different formulas are used [5] for electronic and core-core repulsion integrals. These formulas are very easy to differentiate and are not presented here.

From the Eqs. (1)–(3) and from the proportionality of the resonance and the overlap integral [2–4] in the methods employed it is obvious that the main problem lies in the determination of the derivatives of the overlap and the repulsion integral with respect to the Cartesian coordinates. The overlap integrals were differentiated in a similar way as in Ref. [8] with the use of the formulas of Gerratt and Mills [15]. Since the practical determination of these derivatives and in particular the necessary transformation of the coordinates are very laborious, we give the resultant formulas in Appendix A of this paper. The repulsion integrals were differentiated directly with the use of the corresponding explicit formulas; the results are given in Appendix B. It was found that for practical calculations, where we do not demand an accuracy of the determined coordinates higher than about 10^{-2} Å, it is sufficient to differentiate the repulsion integrals numerically.

In order to study the reactivity, it was indispensable to carry out the minimization in spherical coordinates. The calculation of the geometries of nonequilibrium configurations of the molecule, arising in the formation or in the disappearance of the chemical bond, was performed by means of the fixation of one or more spherical coordinates. This procedure will be described in more detail in the following paper.

The minimization itself was carried out by the variable metric minimization method according to Murtagh and Sargent [14], the necessary formulas for it were taken from Ref. [8]. The calculation began with the conventional CNDO/2 method, which was continued until the average difference in the orbital energies in two successive iterations did not exceed 0.1 eV. Thereupon, the variable metric method was employed as long as the coordinates of the molecule did not change by more than $2 \cdot 10^{-4}$ Å. The control was returned to the CNDO/2 program and the criterion of convergence was halved. The procedure was repeated as long as the average error in the calculation of the orbital energies was larger than 10^{-4} eV. The attainment of self-consistency required about double the number of iterations as were necessary in the case of the simple CNDO/2 calculation. This applies also with the MINDO/2 method.

The program was written in FORTRAN IV for IBM 7040 and IBM 370/155 computers.

Results and Discussion

The usefulness of the method was tested on the formaldehyde molecule. Table 1 presents the results for two different assumed initial geometries in comparison with the calculations by the INDO method [7] and with the experiment [16]. The "exact" equilibrium geometries in both calculations are in agreement with an error of about ± 0.0005 Å in the bond lengths and of 0.4° in the values of the angles. For the sake of comparison the values obtained by the numerical differentiation of repulsion integrals are also presented. It can be noticed that the error is sufficiently small for the study of reaction paths. It was found that already after the first application of the variable metric method, the change in the geometry amounted to 80–90 % of the total change; it is obvious, therefore, that the geometry of the molecule depends rather on the values of the two-centre atomic integrals than on the density matrix. In this way it is possible to explain, e.g., why the CNDO/2 method and the INDO method give so similar estimates of the bond lengths and of the angles.

It is interesting to consider in more detail the CNDO/2 energy contributions of the individual bonds in the equilibrium configuration in the molecule. These

Table 1. Geometry of formaldehyde $H_1H_2C{=}O$ in a ground state

Method	r_{CH_1}	r_{CH_2}	r_{CO}	$\vartheta_{H_1CH_2}$	ϑ_{H_2CO}	ξ[a]	Energy (eV)
1. Initial	0.99	1.00	1.4	90°	135°	10°28′	—
CNDO/2	1.114	1.114	1.247	115°48′	122°6′	0°37′	−730.287
CNDO/2[b]	1.102	1.102	1.234	115°20′	122°20′	0°16′	−730.261
MINDO/2	1.220	1.220	1.204	108°11′	126°	0°20′	−472.112
2. Initial	0.939	1.090	1.238	172°20′	132°40′	0°	—
CNDO/2	1.114	1.114	1.247	115°48′	122°6′	0°	−730.287
INDO[c]	1.12	1.12	1.25	115°	122°30′	0°	—
exp.[d]	1.116	1.116	1.208	116°30′	121°40′	0°	—

[a] $(180-\xi)$ is the angle which bond $C{=}O$ makes with the bisector of H_1–C–H_2.
[b] Numerical differentiation of repulsion integrals was used.
[c] Ref. [7].
[d] Ref. [16].

Table 2. Geometry of formyl radical

Method	r_{CH}	r_{CO}	ϑ_{HCO}	Energy (eV)
Initial	1.2	1.2	120°	—
CNDO/2	1.129	1.223	130°35′	−704.345
CNDO/2[a]	1.106	1.204	130°50′	−704.326
MINDO/2	1.230	1.175	139°30′	−455.353
INDO[b]	1.11	1.22	131°10′	—
Exp.[c]	1.148	1.177	123°20′	—

[a] Numerical differentiation of repulsion integrals was used.
[b] Ref. [7].
[c] Ref. [17].

contributions can be roughly divided into resonance energy, electrostatic attractive (core-electron), and repulsive energy (core-core and electron-electron). The attractive and the repulsive contributions (−522 and +525 eV at the C=O bond) are by an order higher than the resonance energy (−48 eV), but they almost compensate each other, so that the overall energy of the bond is, in principle, the resonance energy. The attractive and the repulsive forces, too, compensate each other to a considerable extent (323 and −375 eV/A for the C=O bond), the contribution of the resonance force is somewhat more significant (53 eV/A). The forces of electrostatic character are inversely proportional to the square of the distance of the atoms; the bond angles are given, in principle by the resonance forces. Consequently it becomes understandable that the extended Hückel method, which neglects the electron repulsion, gives so good estimates of the bond angles.

For testing the open shell minimization procedure we selected the radical HCO. The initial and the final geometries as well as the experimental data are listed in Table 2.

It is known that formaldehyde is non-planar in the first excited singlet state [18], whereas the virtual orbital calculation predicts a planar configuration of the atoms [19].

Our calculations (Table 3) favored the non-planar arrangement of the atoms, in this case the theoretical geometry being in somewhat poorer accordance with

Table 3. Geometry of formaldehyde in excited singlet state

Method	r_{CH}	r_{CO}	ϑ_{HCH}	ξ^a	Energy (eV)
Initial	0.99	1.4	120°	39°30′	—
CNDO/2	1.131	1.287	109°33′	37°35′	−726.498
Exp.[b]	1.093	1.323	119°	31°	—

[a] $(180-\xi)$ is the angle which bond C=O makes with the bisector of H_1–C–H_2.

[b] Ref. [19].

experimental data than for the ground state. The calculated dipole moment is, however, in a good agreement with the experimental one (theor. 1.67 *D*, exp. 1.56 *D*, cf., Ref. [20]). The MINDO/2 applied to the excited state of formaldehyde failed badly for the reaction $H_2CO \rightarrow H_2 + CO$ was predicted to occur without any energy barrier. It is noteworthy that in the unrestricted Hartree-Fock CNDO/2 calculation the energy minimum of the excited state of formaldehyde pertains to the planar molecule (cf., Fig. 2, Ref. [21]).

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Appendix A

Master formulas of the derivatives of the overlap integrals. (Differentiated is always the first member of the pair of the Slater orbitals in the brackets, the differentiation is carried out with respect to the *z* coordinate. The derivatives with respect to the Cartesian coordinates *x* and *y* can be easily ascertained by cyclic interchange of the axes of the coordinate system.)

$$\left\langle \frac{\partial(1s)}{\partial z} \middle| 1s \right\rangle = -(k/\sqrt{3}) \cos\psi \langle 1p_z | 1s \rangle ,$$

$$\left\langle \frac{\partial(1s)}{\partial z} \middle| 2s \right\rangle = -(k/\sqrt{3}) \cos\psi \langle 1p_z | 2s \rangle ,$$

$$\left\langle \frac{\partial(1s)}{\partial z} \middle| 2p_x \right\rangle = -(k/\sqrt{3}) \sin\varphi \sin\psi \cos\psi [\langle 1p_x | 2p_x \rangle + \langle 1p_z | 2p_z \rangle] ,$$

$$\left\langle \frac{\partial(1s)}{\partial z} \middle| 2p_y \right\rangle = -(k/\sqrt{3}) \cos\varphi \sin\psi \cos\psi [\langle 1p_x | 2p_x \rangle + \langle 1p_z | 2p_z \rangle] ,$$

$$\left\langle \frac{\partial(1s)}{\partial z} \middle| 2p_z \right\rangle = -(k/\sqrt{3}) (\cos^2\psi \langle 1p_z | 2p_z \rangle - \sin^2\psi \langle 1p_x | 2p_x \rangle) ,$$

$$\left\langle \frac{\partial(2s)}{\partial z} \middle| 1s \right\rangle = k \cos\psi [(1/3) \langle 1p_z | 1s \rangle - (1/\sqrt{3}) \langle 2p_z | 1s \rangle] ,$$

$$\left\langle \frac{\partial(2p_x)}{\partial z} \middle| 1s \right\rangle = (k/\sqrt{5}) \sqrt{3} \sin\varphi \sin\psi \cos\psi \langle 2d_{z^2} | 1s \rangle ,$$

$$\left\langle \frac{\partial(2p_y)}{\partial z} \middle| 1s \right\rangle = (k/\sqrt{5}) \sqrt{3} \cos\varphi \sin\psi \cos\psi \langle 2d_{z^2} | 1s \rangle ,$$

$$\left\langle \frac{\partial(2p_z)}{\partial z} \middle| 1s \right\rangle = -k \langle 1s | 1s \rangle + (k/\sqrt{3}) \langle 2s | 1s \rangle + (k/\sqrt{15}) (3\cos^2\psi - 1) \langle 2d_{z^2} | 1s \rangle ,$$

$$\left\langle \frac{\partial(2s)}{\partial z} \middle| 2s \right\rangle = k \cos\psi \left[(1/3) \langle 1p_z|2s\rangle - (1/\sqrt{3}) \langle 2p_z|2s\rangle\right] ,$$

$$\begin{aligned}\left\langle \frac{\partial(2s)}{\partial z} \middle| 2p_x \right\rangle = {} & k \sin\varphi \sin\psi \cos\psi [(1/3) (\langle 1p_x|2p_x\rangle + \langle 1p_z|2p_z\rangle) \\ & - (1/\sqrt{3}) (\langle 2p_x|2p_x\rangle + \langle 2p_z|2p_z\rangle)] ,\end{aligned}$$

$$\begin{aligned}\left\langle \frac{\partial(2s)}{\partial z} \middle| 2p_y \right\rangle = {} & k \cos\varphi \sin\psi \cos\psi [(1/3) (\langle 1p_x|2p_x\rangle + \langle 1p_z|2p_z\rangle) \\ & - (1/\sqrt{3}) (2p_x|2p_x\rangle + \langle 2p_z|2p_z\rangle)] ,\end{aligned}$$

$$\begin{aligned}\left\langle \frac{\partial(2s)}{\partial z} \middle| 2p_z \right\rangle = {} & (k/3) (\cos^2\psi \langle 1p_z|2p_z\rangle - \sin^2\psi \langle 1p_x|2p_x\rangle) \\ & - (k/\sqrt{3}) (\cos^2\psi \langle 2p_z|2p_z\rangle - \sin^2\psi \langle 2p_x|2p_x\rangle) ,\end{aligned}$$

$$\left\langle \frac{\partial(2p_x)}{\partial z} \middle| 2s \right\rangle = (k/\sqrt{5}) \sqrt{3} \sin\varphi \sin\psi \cos\psi \langle 2d_{z^2}|2s\rangle ,$$

$$\begin{aligned}\left\langle \frac{\partial(2p_x)}{\partial z} \middle| 2p_x \right\rangle = {} & -(k/\sqrt{5}) \cos\psi [(1 - 2 \sin^2\varphi \sin^2\psi) \langle 2d_{xz}|2p_x\rangle \\ & - \sqrt{3} \sin^2\varphi \sin^2\psi \langle 2d_{z^2}|2p_z\rangle] ,\end{aligned}$$

$$\left\langle \frac{\partial(2p_x)}{\partial z} \middle| 2p_y \right\rangle = (k/\sqrt{5}) \sin\varphi \cos\varphi \sin^2\psi \cos\psi (2 \langle 2d_{xz}|2p_x\rangle + \sqrt{3} \langle 2d_{z^2}|2p_z\rangle) ,$$

$$\begin{aligned}\left\langle \frac{\partial(2p_x)}{\partial z} \middle| 2p_z \right\rangle = {} & (k/\sqrt{5}) \sin\varphi \sin\psi [(\cos^2\psi - \sin^2\psi) \langle 2d_{xz}|2p_x\rangle \\ & + \sqrt{3} \cos^2\psi \langle 2d_{z^2}|2p_z\rangle] ,\end{aligned}$$

$$\left\langle \frac{\partial(2p_y)}{\partial z} \middle| 2s \right\rangle = (k/\sqrt{5}) \sqrt{3} \cos\varphi \sin\psi \cos\psi \langle 2d_{z^2}|2s\rangle ,$$

$$\left\langle \frac{\partial(2p_y)}{\partial z} \middle| 2p_x \right\rangle = (k/\sqrt{5}) \sin\varphi \cos\varphi \sin^2\psi \cos\psi (2 \langle 2d_{xz}|2p_x\rangle + \sqrt{3} \langle 2d_{z^2}|2p_z\rangle) ,$$

$$\begin{aligned}\left\langle \frac{\partial(2p_y)}{\partial z} \middle| 2p_y \right\rangle = {} & -(k/\sqrt{5}) \cos\psi [(1 - 2 \sin^2\varphi \sin^2\psi) \langle 2d_{xz}|2p_x\rangle \\ & + \sqrt{3} \cos^2\varphi \sin^2\psi \langle 2d_{z^2}|2p_z\rangle] ,\end{aligned}$$

$$\begin{aligned}\left\langle \frac{\partial(2p_y)}{\partial z} \middle| 2p_z \right\rangle = {} & (k/\sqrt{5}) \cos\varphi \sin\psi [(\cos^2\psi - \sin^2\psi) \langle 2d_{xz}|2p_x\rangle \\ & + \sqrt{3} \cos^2\psi \langle 2d_{z^2}|2p_z\rangle] ,\end{aligned}$$

$$\left\langle \frac{\partial(2p_z)}{\partial z} \middle| 2s \right\rangle = -k \langle 1s|2s\rangle + (k/\sqrt{3}) \langle 2s|2s\rangle + (k/\sqrt{15}) (3 \cos^2\psi - 1) \langle 2d_{z^2}|2s\rangle ,$$

$$\begin{aligned}\left\langle \frac{\partial(2p_z)}{\partial z} \middle| 2p_x \right\rangle = {} & -k \sin\varphi \sin\psi [\langle 1s|2p_z\rangle - (1/\sqrt{3}) \langle 2s|2p_z\rangle] \\ & + (2k/\sqrt{15}) \sin\varphi \sin\psi [\sqrt{3} \cos^2\psi \langle 2d_{xz}|2p_x\rangle \\ & + (1/2) (3 \cos^2\psi - 1) \langle 2d_{z^2}|2p_z\rangle] ,\end{aligned}$$

$$\begin{aligned}\left\langle \frac{\partial(2p_z)}{\partial z} \middle| 2p_y \right\rangle = {} & -k \cos\varphi \sin\psi [\langle 1s|2p_z\rangle - (1/\sqrt{3}) \langle 2s|2p_z\rangle] \\ & + (2k/\sqrt{15}) \cos\varphi \sin\psi [\sqrt{3} \cos^2\psi \langle 2d_{xz}|2p_x\rangle \\ & + (1/2) (3 \cos^2\psi - 1) \langle 2d_{z^2}|2p_z\rangle] ,\end{aligned}$$

$$\begin{aligned}\left\langle \frac{\partial(2p_z)}{\partial z} \middle| 2p_z \right\rangle = {} & -k \cos\psi [\langle 1s|2p_z\rangle - (1/\sqrt{3}) \langle 2s|2p_z\rangle] \\ & - (2k/\sqrt{15}) \cos\psi [\sqrt{3} \sin^2\psi \langle 2d_{xz}|2p_x\rangle - (1/2) \\ & \cdot (3 \cos^2\psi - 1) \langle 2d_{z^2}|2p_z\rangle]\end{aligned}$$

where k is the Slater exponent of the differentiated orbital, the Euler angles are defined as follows (the differentiated orbital has the coordinates x_1, y_1, z_1):

$$\begin{aligned}
&\sin\varphi = \frac{\Delta x}{r}, \quad && \sin\psi = \frac{r}{R}, \quad && r^2 = \Delta x^2 + \Delta y^2, \\
& && && R^2 = r^2 + \Delta z^2 \\
&\cos\varphi = \frac{\Delta y}{r}, && \cos\psi = \frac{\Delta z}{R}, && \Delta x = x_1 - x_2 \\
& && && \Delta y = y_1 - y_2 \\
& && && \Delta z = z_1 - z_2 \,.
\end{aligned}$$

Appendix B

Differentiation of the bicentric repulsion integrals with respect to the Cartesian coordinates

$$\frac{\partial \gamma_{\mathrm{AB}}}{\partial x_{\mathrm{A}}} = 27.20974\, G \frac{x_{\mathrm{A}} - x_{\mathrm{B}}}{d}\,.$$

Case 1: $s = \sigma$

$$\begin{aligned}
G(1s, 1s) = \frac{1}{d}\Big\{ -\frac{1}{d} + e^{-2sd}\Big[\Big(1 + \frac{11}{8} sd + \frac{3}{4} s^2 d^2 + \frac{1}{6} s^3 d^3\Big)\Big(\frac{1}{d} + 2s\Big) \\
- \frac{11}{8} s - \frac{3}{2} s^2 d - \frac{1}{2} s^3 d^2\Big]\Big\},
\end{aligned}$$

$$\begin{aligned}
G(1s, 2s) = \frac{1}{d}\Big\{ -\frac{1}{d} + e^{-2sd}\Big[\Big(1 + \frac{25}{16} sd + \frac{9}{8} s^2 d^2 + \frac{23}{48} s^3 d^3 \\
+ \frac{1}{8} s^4 d^4 + \frac{1}{60} s^5 d^5\Big)\Big(\frac{1}{d} + 2s\Big) - \frac{25}{16} s - \frac{9}{4} s^2 d - \frac{23}{16} s^3 d^2 \\
- \frac{1}{2} s^4 d^3 - \frac{1}{12} s^5 d^4\Big]\Big\},
\end{aligned}$$

$$\begin{aligned}
G(2s, 2s) = \frac{1}{d}\Big\{ -\frac{1}{d} + e^{-2sd}\Big[\Big(1 + \frac{419}{256} sd + \frac{163}{128} s^2 d^2 + \frac{119}{192} s^3 d^3 \\
+ \frac{5}{24} s^4 d^4 + \frac{1}{20} s^5 d^5 + \frac{1}{120} s^6 d^6 + \frac{1}{1260} s^7 d^7\Big)\Big(\frac{1}{d} + 2s\Big) \\
- \frac{419}{256} s - \frac{163}{64} s^2 d - \frac{163}{64} s^2 d - \frac{119}{64} s^3 d^2 - \frac{5}{6} s^4 d^3 - \frac{1}{4} s^5 d^4 \\
- \frac{1}{20} s^6 d^5 - \frac{1}{180} s^7 d^6\Big]\Big\}.
\end{aligned}$$

Case 2: $s \neq \sigma$

$$\begin{aligned}
G(1s, 1s) = \frac{1}{d}\Big\{ -\frac{1}{d} + n^2 e^{-2sd}\Big[\frac{2 + a + sd}{4}\Big(\frac{1}{d} + 2s\Big) - \frac{s}{4}\Big] \\
+ b^2 e^{-2\sigma d}\Big[\frac{2 - a + \sigma d}{4}\Big(\frac{1}{d} + 2\sigma\Big) - \frac{\sigma}{4}\Big]\Big\},
\end{aligned}$$

$$\begin{aligned}
G(1s, 2s) = \frac{1}{d}\Big\{ -\frac{1}{d} + n^3 e^{-2sd}\Big[\Big(\frac{1 - 5a - 4a^2}{16} - \frac{asd}{8}\Big)\Big(\frac{1}{d} + 2s\Big) + \frac{as}{8}\Big] \\
+ b^2 e^{-2\sigma d}\Big[\Big(\frac{15 - 22a + 15a^2 - 4a^3}{16} + 3\,\frac{3 - 3a + a^2}{8}\sigma d + \frac{2 - a}{4}\sigma^2 d^2 \\
+ \frac{\sigma^3 d^3}{12}\Big)\Big(\frac{1}{d} + 2\sigma\Big) - 3\,\frac{3 - 3a + a^2}{8}\sigma - \frac{2 - a}{2}\sigma^2 d - \frac{\sigma^3 d^2}{4}\Big]\Big\},
\end{aligned}$$

$$\begin{aligned} G(2s,2s) = \frac{1}{d}\Bigg\{ & -\frac{1}{d} + n^3 e^{-2sd} \left[\left(\frac{8-a-27a^2-30a^3-10a^4}{16} + \frac{11-19a-44a^2-20a^3}{32}\right.\right. \\ & \left.\cdot sd + \frac{1-5a-4a^2}{16} s^2 d^2 - \frac{a}{24} s^3 d^3\right)\left(\frac{1}{d}+2s\right) - \frac{11-19a-44a^2-20a^3}{32} s \\ & \left. - \frac{1-5a-4a^2}{8} s^2 d + \frac{a}{8} s^3 d^2\right] + b^3 e^{-2\sigma d}\left[\left(\frac{8+a-27a^2+30a^3-10a^4}{16}\right.\right. \\ & \left. + \frac{11+19a-44a^2+20a^3}{32}\sigma d + \frac{1+5a-4a^2}{16}\sigma^2 d^2 + \frac{a}{24}\sigma^3 d^3\right)\left(\frac{1}{d}+2\sigma\right) \\ & \left.\left. - \frac{11+19a-44a^2+20a^3}{32}\sigma - \frac{1+5a-4a^2}{8}\sigma^2 d - \frac{a}{8}\sigma^3 d^2\right]\right\} \end{aligned}$$

where x_A and x_B are coordinates of atoms, s, σ are Slater exponents, d is the distance of the atoms in atomic units, $a=0.5(t+1/t)$, $b=1+a$, $n=1-a$, $t=\frac{s-\sigma}{s+\sigma}$.

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