The contribution to the 1s-orbital energy is five to ten times greater than that to the 2s-orbital energy. For single electrons in doubly filled orbitals, the relativistic corrections are approximately:

$$E_{\rm rel}(1s) \approx 0.116_8\alpha^2(Z - .534)^4 , \qquad (9a)$$

$$E_{\rm rel}(2s) \approx 0.0402\alpha^2(Z - 2.1_0)^4 , \qquad (9b)$$

$$E_{\rm rel}(2p) \approx 0.0402\alpha^2(Z - 6.6_5)^4 . \qquad (9c)$$

These values appear in Table VII together with the results of Pekeris[12] and Scherr *et al.*[11] from which they were derived. (These contain the implicit assumption, only true to first order, that the correction for an inner electron is independent of the presence of an outer one.)

The additivity of pair correlation effects here demonstrated by the analysis of instrumental and computational experiments on atomic systems is of first importance to contemporary formulations of the many-electron problem in atoms and molecules. The traditional method of configuration interaction is most efficiently carried through and interpreted under the assumption of additivity.[31] In addition to other factors, successful utilization of the recent formulations of Sinanoğlu,[19,32] Szász,[33] and Tsang[34] depends upon the separability and additivity of pair correlations. A description of correlation in terms of opposite spin pairs is also inherent to the method of spin-correlated orbitals.[35] Further, it seems evident that, in the generalized self-consistent-field theory of McWeeny,[36] the localized electron groups which are to be treated exactly should be groups of two orbital partners. The present analysis also suggests, for calculations in the near future, the additional approximation of neglecting all correlations except those between orbitally paired electrons. Such a treatment would account for more than 80% of the total correlation energy.

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Nonadiabatic Theory for Diatomic Molecules and Its Application to the Hydrogen Molecule*

W. Kołos†
Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago, Illinois

AND

L. Wolniewicz
Department of Theoretical Physics, Nicholas Copernicus University, Toruń, Poland

1. INTRODUCTION

ONE of the most fundamental approximations[1] of the theory of molecular structure consists of separating the nuclear motion and in computing only the electronic wave functions and energies for fixed positions of the nuclei. This is the socalled adiabatic approximation which is applicable, if the motion of the nuclei is much slower than that of the electrons. In the mathematical formulation of this approximation, the total wave function is assumed in the form of a product both of whose factors can be computed as solutions of two separate Schrödinger equations.

In most applications the separation is valid with sufficient accuracy, and the adiabatic approach is extremely valuable, especially if the electronic properties of molecules are considered. However, as

* Supported in part by the National Science Foundation.
† Permanent and present address: Institute of Nuclear Research, Polish Academy of Sciences, Warsaw, Poland.
[1] M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).

is shown in the next section, the method becomes rather impracticable if the vibrational wave functions are needed, and it seems that in these cases a direct computation of the complete electronic–vibrational wave function is more appropriate. This happens when one is interested in computing expectation values of the operators which explicitly depend on the nuclear coordinates, e.g., the internuclear distances, moments of inertia, etc. The vibrational wave functions are also needed in accurate computations of those quantities which parametrically depend on the nuclear coordinates. Suppose, for example, that we want to compute the dipole or the quadrupole moment of a diatomic molecule. In the adiabatic approximation, one has first to compute the moment as a function of the internuclear distance and then to average it over the zero-point vibrations. The averaging can obviously be performed if the vibrational wave function is known, however, one can avoid the intermediate step and compute the moment directly, if a complete electronic–vibrational wave function is available.

There are also some important cases in which the adiabatic approximation does not yield sufficiently accurate energy values. Thus the approximation is certainly inadequate when employed to the μ-mesonic molecular systems, or to the hydrogen molecule for which the experimental measurements,[2] as well as the theoretical clamped nuclei computations,[3] have recently reached such a high degree of precision that a refinement of the theory is undoubtedly desirable. In addition, a nonadiabatic energy calculation has the advantage of giving directly the observable dissociation energy of the molecule and not the potential energy curve.

In the following section the adiabatic approximation is briefly discussed, and its defects are pointed out. A nonadiabatic method of treating diatomic molecules is developed in Sec. 3, and, in the subsequent section, the method is applied to two-electron molecules, i.e., to four-particle molecular systems. Methods of this type have been previously employed[4] to three-particle systems, such as the electronic and mesonic hydrogen ions. The last section contains some numerical results obtained in the nonadiabatic approximation for the ground state of the hydrogen molecule.

[2] G. Herzberg and A. Monfils, J. Mol. Spectr. **5**, 482 (1960).

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2. THE ADIABATIC APPROXIMATION

In the theory of molecular structure the adiabatic approximation can be obtained in two different ways, yielding different results. The first method is due to Born and Oppenheimer[1] and the second has been given later by Born.[5] Let us briefly discuss both methods, as applied to diatomic molecules.

As is well known the Born–Oppenheimer approach is a consequent perturbation treatment based on the smallness of the electron mass m with respect to the masses of the nuclei, and on the assumption that the expansion parameter κ satisfies the relation $\kappa a \sim b$, where a is the linear dimension of the molecule, and b the amplitude of the nuclear vibrations. Hence, $\kappa = (m/\mu)^{\frac{1}{4}}$, where μ denotes the reduced mass of the two nuclei.[6]

By expanding the wave function and the energy of the molecule it has been shown[1] that in this approach the adiabatic approximation is valid only up to terms of the order of κ^2 in the wave function, and of the order of κ^4 in the energy. In the case of large μ (i.e., small κ) this accuracy is obviously sufficient, however, the main defect of the Born–Oppenheimer procedure consists in the practical impossibility of increasing the accuracy of the calculations, which is of importance if μ is relatively small, or if high accuracy of the results is desired.

Now let us sum up the main points of the Born method. The exact Hamiltonian of the molecule in the center of mass system[7] is separated into two parts

$$H = H_0 + H' , \tag{1}$$

where H_0 denotes the Hamiltonian in the clamped nuclei approximation including the nuclear repulsion, and H' describes the kinetic energy of the relative motion of the two nuclei, as well as the coupling between the electronic and the nuclear motions.[8]

[5] M. Born, Nachr. Akad. Wiss. Göttingen 1 (1951); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1956).

[6] Since Born and Oppenheimer were interested only in estimation of the orders of magnitude of the various corrections they took μ as any one of the nuclear masses or their mean, and the actual choice was immaterial for the estimation.

[7] The separation can also be performed in other coordinate systems, cf. D. W. Jepsen and J. O. Hirschfelder, J. Chem. Phys. **32**, 1323 (1960); A. Fröman, J. Chem. Phys. **36**, 1490 (1962).

[8] For the H_2 molecule the diagonal elements C_{nn} have been computed, although not very accurately, by J. H. Van Vleck, J. Chem. Phys. **4**, 327 (1936); A. Dalgarno and R. McCarroll, Proc. Roy Soc. (London) **A237**, 383 (1956); **A239**, 413 (1957); W. Kołos and L. Wolniewicz, Acta Phys. Polon. **20**, 129 (1961).

The electronic problem

$$H_0\psi_n(x,R) = U_n(R)\psi_n(x,R) \qquad (2)$$

is assumed to be solved. In (2) x represents the coordinates of all electrons in the molecule, $R = |\mathbf{R}|$, and $\mathbf{R}$ is the relative position vector of the nuclei. The electronic wave functions $\psi_n(x,R)$ are chosen to be real and normalized for all values of the parameter R. Obviously they form a complete set in the space of x. Now one looks for the solution of the problem

$$(H_0 + H')\Psi(x,\mathbf{R}) = E\Psi(x,\mathbf{R}) \qquad (3)$$

in the form of the expansion

$$\Psi(x,\mathbf{R}) = \textstyle\sum_n \mathrm{X}_n(\mathbf{R})\psi_n(x,R) \ , \qquad (4)$$

which gives the following rigorous set of equations for the functions $\mathrm{X}_n(\mathbf{R})$

$$\left\{-\frac{\hbar^2}{2\mu}\Delta_{\mathbf{R}} + U_n(R) + C_{nn} - E\right\}\mathrm{X}_n(\mathbf{R}) = -\sum_{n'\neq n} C_{n'n}\mathrm{X}_{n'}(\mathbf{R}) \ , \qquad (5)$$

where

$$C_{n'n} = \int \psi_{n'}(x,R)H'\psi_n(x,R)dx \ .$$

The operators $C_{n'n}$ have the form

$$C_{n'n} = A_{n'n}(R) + (1 - \delta_{n'n})\mathbf{B}_{n'n}(R)\nabla_R \ ,$$

Now, if one neglects the right-hand side of (5), one gets the adiabatic approximation, $\Psi = \psi_n\mathrm{X}_n$, and a Schrödinger-type equation for the vibrational wave function

$$\left\{-\frac{\hbar^2}{2\mu}\Delta_{\mathbf{R}} + U_n'(R) - E\right\}\mathrm{X}_n(\mathbf{R}) = 0 \ . \qquad (6)$$

The diagonal element C_{nn}, which is a function of R only, can be interpreted as a correction to the potential energy $U_n(R)$, due to the coupling between the electronic and the nuclear motions,[8] and therefore, in (6), C_{nn} has been incorporated into $U_n'(R)$. If, in the adiabatic approximation, the vibrational wave functions are needed one has to solve Eq. (6) with the troublesome numerical potential $U_n'(R)$ [or $U_n(R)$ in the Born–Oppenheimer method].

The main advantage of the Born method, as compared with the original Born–Oppenheimer approach, consists, in our opinion, in the fact that it enables us to compute the correction term C_{nn} and thus the "best possible" potential energy curve for nuclear vibrations. In addition, contrary to the earlier Born–Oppenheimer approach, the method avoids the assumption that the amplitude of vibrations is small compared to the internuclear distance. Unfortunately, the separation of the wave function is not uniquely defined,[7] and, in the practically soluble adiabatic approximation, the accuracy of the method is not well determined. It is obvious that this approximation is valid, if there is no overlap between the electronic wave functions $\psi_n(x,R)$; however, in a general case, it is not possible to estimate quantitatively the accuracy of the method.

The criticism applies especially to the computation of the wave function, which, when assumed in the form of the product $\Psi = \psi_n\mathrm{X}_n$, may appreciably deviate from the accurate solution of the problem. It is true that in both methods discussed above one can, in principle, solve the problem accurately, however, the computation would be prohibitively complex and laborious, and neither of the methods is practical for high-accuracy computations. In both cases the complete set of the electronic wave functions $\psi_n(x,R)$ would be needed and, e.g., in the Born method, one would have to solve the set of Eqs. (5).

Thus, in our opinion, if one is interested in more accurate results than those which can be obtained in the adiabatic approximation, one should not try to improve this approximation. Instead one should rather drop from the very beginning the idea of separation of the electronic and nuclear motions, and start with the exact Schrödinger equation for all the particles involved. This approach has been adopted in the present work.

3. THE SCHRÖDINGER EQUATION FOR THE RELATIVE MOTION

In this section we give the Schrödinger equation for the relative motion of the electrons and nuclei in a diatomic molecule, after separating off the center of mass motion and the rotations.

Let us denote the coordinates and masses of the two nuclei in a fixed reference system by $\mathbf{R}_A$, $\mathbf{R}_B$, and M_A, M_B, respectively, and the electronic coordinates by $\boldsymbol{\xi}_i(i = 1,2,\cdots,N)$, N being the number of electrons. The separation of the center of mass motion is straightforward. In the center of mass system S', with space fixed axes X',Y',Z', the Hamiltonian, in atomic units, reads

$$H = H_0 + H' \ ,$$
$$H_0 = -\tfrac{1}{2}\textstyle\sum_j \Delta_{\mathbf{r}_j} + V \ , \qquad (7)$$
$$H' = -\frac{m}{2\mu}\Delta_{\mathbf{R}} - \frac{m}{8\mu}\left(\sum_j \nabla_{\mathbf{r}_j}\right)^2 - \frac{m}{2\mu_a}\nabla_{\mathbf{R}}\sum_j \nabla_{\mathbf{r}_j} \ ,$$

where

$$\mu = \frac{M_A M_B}{M_A + M_B}, \qquad \mu_a = \frac{M_A M_B}{M_A - M_B},$$

and the coordinates are:

$$\mathbf{R} = \mathbf{R}_A - \mathbf{R}_B\,, \quad \mathbf{r}_j = \boldsymbol{\xi}_j - \tfrac{1}{2}(\mathbf{R}_A + \mathbf{R}_B)\,.$$

To separate the rotations, let us consider the following operators:

$\mathbf{K}^2$—the square of the angular momentum of the system in S',

$K_{Z'}$—the component of $\mathbf{K}$ in the direction of a fixed axis Z',

$(1/R)\mathbf{RK}$—the component of $\mathbf{K}$ in the direction of the molecular axis, which will be called the Z direction.

Since

$$\mathbf{K} = -i\mathbf{R} \times \nabla_{\mathbf{R}} + \mathbf{L}\,,$$

where $\mathbf{L}$, is the electronic angular momentum

$$\mathbf{L} = -i \textstyle\sum_j \mathbf{r}_j \times \nabla_{\mathbf{r}_j}\,,$$

one finds

$$(1/R)\mathbf{RK} = L_Z\,. \tag{8}$$

From the axial symmetry of the problem it follows that the orthonormal eigenfunctions of the operators $\mathbf{K}^2$, $K_{Z'}$ and L_z are the wave functions of a symmetric top. Let us denote these functions by $\Omega^K_{M_K,\Lambda}$ where K, M_K and Λ are the eigenvalues of the $\mathbf{K}^2$, $K_{Z'}$ and L_Z operators, respectively. It is well known[9] that any solution of the equation

$$H\Psi = E\Psi \tag{9}$$

with definite quantum numbers K and M_K can be represented by

$$\Psi = \sum_{\Lambda=-K}^{K} \Omega^K_{M_K,\Lambda} u^K_\Lambda\,, \tag{10}$$

where the functions u^K_Λ depend only on the relative positions of the particles. On substitution of (10) into (9), one can eliminate from the Schrödinger equation the rotational degrees of freedom. The set of equations for the u^K_Λ functions which will be obtained in this way describes the internal motions of the molecule. This procedure is obviously equivalent to a transformation of the Hamiltonian (7) to a representation in which the operators $\mathbf{K}^2$, $K_{Z'}$ and L_Z are diagonal. Since L_Z does not commute with H', the Hamiltonian in this representation will have a nondiagonal form.

To perform the operations indicated above it is convenient to express R in the polar coordinate system R, θ, φ, and to introduce a rotating reference system S, specified as follows: The Z axis has the direction of $\mathbf{R}$, the Y axis is perpendicular to both Z, and the fixed direction Z', and X is perpendicular to Y and Z, and XYZ form a right-handed system.

Now if we denote by x_j', y_j', z_j' and x_j, y_j, z_j the components of $\mathbf{r}_j$ in S' and S, respectively, the transformation from S' to S is:

$$\begin{pmatrix} x_j \\ y_j \\ z_j \end{pmatrix} = \begin{pmatrix} \cos\theta\cos\varphi, & \cos\theta\sin\varphi, & -\sin\theta \\ -\sin\varphi, & \cos\varphi, & 0 \\ \sin\theta\cos\varphi, & \sin\theta\sin\varphi, & \cos\theta \end{pmatrix} \begin{pmatrix} x_j' \\ y_j' \\ z_j' \end{pmatrix}, \tag{11}$$

R, θ, φ remaining unchanged. It is obvious, that (11) leaves the Hamiltonian (7) unaltered, except the operators $\Delta_{\mathbf{R}}$ and $\nabla_{\mathbf{R}}\cdot\sum\nabla_{\mathbf{r}_j}$, which now read

$$\begin{aligned}
\Delta_{\mathbf{R}} = {} & \frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\left\{\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\} \\
& + \frac{1}{R^2}\left\{L_Z - L^+L^- - \cot^2\theta L_Z^2 - 2i\frac{\cot\theta}{\sin\theta}L_Z\frac{\partial}{\partial\varphi}\right\} \\
& + \frac{1}{R^2}L^+\left\{-\frac{\partial}{\partial\theta} + \cot\theta L_Z + \frac{i}{\sin\theta}\frac{\partial}{\partial\varphi}\right\} \\
& + \frac{1}{R^2}L^-\left\{\frac{\partial}{\partial\theta} + \cot\theta L_Z + \frac{i}{\sin\theta}\frac{\partial}{\partial\varphi}\right\},
\end{aligned} \tag{12}$$

$$\begin{aligned}
\nabla_{\mathbf{R}}\sum\nabla_{\mathbf{r}_j} = {} & iP_Z\frac{\partial}{\partial R} + \frac{i}{2R}(P^+L^- - P^-L^+) \\
& + \frac{i}{2R}P^+\left(\frac{\partial}{\partial\theta} - \frac{i}{\sin\theta}\frac{\partial}{\partial\varphi} - \cot\theta L_Z\right) \\
& + \frac{i}{2R}P^-\left(\frac{\partial}{\partial\theta} + \frac{i}{\sin\theta}\frac{\partial}{\partial\varphi} + \cot\theta L_Z\right),
\end{aligned} \tag{13}$$

where

$$L^\pm = L_X \pm iL_Y\,, \quad P^\pm = P_X \pm iP_Y\,,$$

and L_X, L_Y, L_Z and P_X, P_Y, P_Z are the components of the electronic angular momentum, and of the impulse operator $\mathbf{P} = -i\sum_j \nabla_{\mathbf{r}_j}$ respectively in the rotating reference system S.

Note, that in (12) and below the differentiation with respect to θ or φ means a differentiation with fixed x_j, y_j, z_j.

Now we choose for simplicity the electronic coordinates in such a way, that the angle ψ, describing a simultaneous rotation of the electrons around Z is

[9] E. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York and London, 1959).

an independent variable [see (19a)], and we get

$$L_Z = -i(\partial/\partial\psi) . \quad (14)$$

Obviously, φ, θ, ψ are the Eulerian angles of the molecule. So $\Omega^K_{M_K,\Lambda}$ can be written in the form[9]

$$\Omega^K_{M_K,\Lambda} = \frac{1}{2\pi} e^{iM_K\varphi} e^{i\Lambda\psi} \vartheta^K_{M_K,\Lambda}(\theta) . \quad (15)$$

The explicit form of $\vartheta^K_{M_K,\Lambda}$, and its properties, which will be needed in the following are put together in the Appendix A.

Now we can easily eliminate from (9) the angles φ, θ, and ψ. Since H is diagonal in K and M_K it will be convenient to drop these indices, and the matrix elements will be simply written in the form

$$\langle K,M_K,\Lambda'|H|K,M_K,\Lambda\rangle \equiv \langle\Lambda'|H|\Lambda\rangle \equiv H_{\Lambda'\Lambda} .$$

Keeping in mind the well-known properties of the operators $\mathbf{L}$ and $\mathbf{P}$ one easily sees, that the only nondiagonal terms in H are those, which are proportional to one (and only one) of the four operators $L^\pm$, $P^\pm$. Next, since the matrix elements of these operators vanish unless $\Lambda' = \Lambda \pm 1$, one has

$$H_{\Lambda'\Lambda} = 0 \quad \text{if } \Lambda' \neq \Lambda \text{ and } \Lambda' \neq \Lambda \pm 1 . \quad (16)$$

The nonvanishing elements can be found by making use of (7), (12), (13), and of the properties (A.1), (A.2), (A.3) of the functions $\vartheta^K_{M_K,\Lambda}$:

$$\begin{aligned} H_{\Lambda\Lambda} = &-\tfrac{1}{2} \textstyle\sum_j \langle\Lambda|\Delta_{\mathbf{r}_j}|\Lambda\rangle + V + \frac{m}{8\mu}\langle\Lambda|\mathbf{P}^2|\Lambda\rangle \\ &-\frac{m}{2\mu}\left\{\frac{\partial^2}{\partial R^2} + \frac{2}{R}\frac{\partial}{\partial R} - \frac{K(K+1)-\Lambda(\Lambda+1)}{R^2} - \frac{1}{R^2}\langle\Lambda|L^+L^-|\Lambda\rangle\right\} \\ &-\frac{im}{2\mu_a}\left\{P_Z\frac{\partial}{\partial R} + \frac{1}{2R}\langle\Lambda|P^+L^- - P^-L^+|\Lambda\rangle\right\} \quad (17) \end{aligned}$$

$$H_{\Lambda+1,\Lambda} = [(K+\Lambda+1)(K-\Lambda)]^{\frac{1}{2}} \times \left\{\frac{m}{2\mu R^2}\langle\Lambda+1|L^+|\Lambda\rangle - \frac{im}{4\mu_a R}\langle\Lambda+1|P^+|\Lambda\rangle\right\},$$

$$H_{\Lambda-1,\Lambda} = [(K+\Lambda)(K-\Lambda+1)]^{\frac{1}{2}} \times \left\{\frac{m}{2\mu R^2}\langle\Lambda-1|L^-|\Lambda\rangle + \frac{im}{4\mu_a R}\langle\Lambda-1|P^-|\Lambda\rangle\right\} .$$

The matrix elements of the electronic operators, e.g., of $\langle\Lambda'|P^+|\Lambda\rangle$, are operators acting on the internal coordinates of the molecule, and obviously their form depends on the choice of these coordinates. For the special two-electron case we give them explicitly in the Appendix B.

However, independently of the form of the electronic operators it is seen from (16) and (17) that the exact Schrödinger equation of a diatomic molecule with definite K is given by a set of $2K+1$ equations for the $2K+1$ components u_Λ of the wave function:

$$H_{\Lambda\Lambda}u_\Lambda + H_{\Lambda,\Lambda-1}u_{\Lambda-1} + H_{\Lambda,\Lambda+1}u_{\Lambda+1} = Eu_\Lambda , \quad \Lambda = -K, -K+1, \cdots, K . \quad (18)$$

This is the required equation for the internal motion. Obviously both, the eigenvalue E and the components u_Λ depend on the angular momentum K

$$E = E_K , \quad u_\Lambda = u_\Lambda^K ,$$

and u_Λ are functions of the internuclear distance R, and of the $3N-1$ electronic coordinates.

As yet, the solutions of (18) are not uniquely defined, as there exists an operator, which commutes with both, the Hamiltonian H, and the angular momentum $\mathbf{K}$. This is the inversion I

$$\mathbf{R} \to -\mathbf{R},\ x_j' \to -x_j',\ y_j' \to -y_j',\ z_j' \to -z_j' .$$

To find the conditions to be fulfilled by u_Λ to assure a definite parity of the state with respect to I, we shall describe for definiteness the positions of the electrons in S by means of the elliptic coordinates ξ_i, η_i with respect to R, and the azimuthal angles ψ_i ($i = 1,2,\cdots,N$). Thus, the internal coordinates occurring in u_Λ can be chosen as

$$R,\ \xi_i,\ \eta_i\ (i = 1,2,\cdots,N) , \quad \text{and } \phi_j \quad (j = 1,2,\cdots,N-1) , \quad (19)$$

where $\phi_j = \psi_j - \psi_{j+1}$, and the simultaneous rotation of the electrons is described by

$$\psi = (1/N)(\psi_1 + \psi_2 + \cdots + \psi_N) . \quad (19a)$$

From (11) it is seen, that in the moving reference system S, the inversion I reads:

$$R \to R , \quad \theta \to \pi - \theta , \quad \varphi \to \pi + \varphi, \quad x_j \to -x_j , \quad y_j \to y_j , \quad z_j \to z_j ,$$

and remembering the definition of the elliptic coordinates we can write it as

$$R \to R , \quad \theta \to \pi - \theta , \quad \varphi \to \pi + \varphi , \quad \xi_i \to \xi_i , \quad \eta_i \to \eta_i , \quad \phi_j \to -\phi_j , \quad \psi \to \pi - \psi .$$

Thus, due to (10) and (15), we have

$$\begin{aligned} I\Psi_{K,M_K}&(\theta,\varphi,\psi;R,\xi_i,\eta_i,\phi_j) \\ &= \frac{1}{2\pi} e^{iM_K\varphi} \sum_\Lambda (-1)^{M_K+\Lambda} u_\Lambda(R,\xi_i,\eta_i,-\phi_j) \times e^{-i\Lambda\psi}\vartheta^K_{M_K\Lambda}(\pi-\theta) . \quad (20) \end{aligned}$$

If we now define the symmetric $\Psi^s_{KM_K}$ and antisymmetric $\Psi^a_{KM_K}$ functions by

$$I\Psi^s_{KM_K} = (-1)^K\Psi^s_{KM_K}, \quad I\Psi^a_{KM_K} = -(-1)^K\Psi^a_{KM_K}$$

and make use of (A.5) we get from (20) the following conditions for u^s_Λ and u^a_Λ:

$$u^s_\Lambda(R,\xi_i,\eta_i,\phi_j) = (-1)^\Lambda u^s_{-\Lambda}(R,\xi_i,\eta_i,-\phi_j),$$
$$u^a_\Lambda(R,\xi_i,\eta_i,\phi_j) = -(-1)^\Lambda u^a_{-\Lambda}(R,\xi_i,\eta_i,-\phi_j). \quad (21)$$

To the end of this section we shall briefly discuss the wave function of a molecule with identical nuclei. In this case the Hamiltonian is additionally invariant on the inversion I_n of the nuclei alone.[10]

In terms of the coordinates (19) this inversion reads:

$$R \to R, \quad \theta \to \pi - \theta, \quad \varphi \to \pi + \varphi,$$
$$\xi_i \to \xi_i, \quad \eta_i \to -\eta_i, \quad \phi_j \to -\phi_j, \quad \psi \to -\psi.$$

With the definition

$$I_n{}^s\Psi_{KM_K} = (-1)^{K^s}\Psi_{KM_K},$$
$$I_n{}^a\Psi_{KM_K} = -(-1)^{K^a}\Psi_{KM_K},$$

one finds now

$${}^s u_\Lambda(R,\xi_i,\eta_i,\phi_j) = {}^s u_{-\Lambda}(R,\xi_i,-\eta_i,-\phi_j),$$
$${}^a u_\Lambda(R,\xi_i,\eta_i,\phi_j) = -{}^a u_{-\Lambda}(R,\xi_i,-\eta_i,-\phi_j). \quad (22)$$

Combining (21) and (22) we get readily

$${}^s u^s_\Lambda(R,\xi_i,\eta_i,\phi_j) = (-1)^{\Lambda s}\, {}^s u^s_\Lambda(R,\xi_i,-\eta_i,\phi_j),$$
$${}^a u^a_\Lambda(R,\xi_i,\eta_i,\phi_j) = (-1)^{\Lambda a}\, {}^a u^a_\Lambda(R,\xi_i,-\eta_i,\phi_j),$$
$${}^s u^a_\Lambda(R,\xi_i,\eta_i,\phi_j) = -(-1)^{\Lambda s}\, {}^s u^a_\Lambda(R,\xi_i,-\eta_i,\varphi_j), \quad (23)$$
$${}^a u^s_\Lambda(R,\xi_i,\eta_i,\phi_j) = -(-1)^{\Lambda a}\, {}^a u^s_\Lambda(R,\xi_i,-\eta_i,\phi_j),$$

where, for example, ${}^s u^a_\Lambda$ is a component of a wave function, which is symmetric with respect to I_n and antisymmetric with respect to I.

The relations (21)–(23) facilitate the choice of the trial functions, if the exact Eqs. (18) are to be solved numerically.

4. DIATOMIC TWO-ELECTRON MOLECULES

The theory presented in the preceding section will now be applied to perform a variational calculation for the ground state of a diatomic two-electron molecule. From the set of Eqs. (18) one gets for $K = 0$ one equation for the wave function[11] $\Psi = u_0$, which, according to (21) has a definite symmetry with respect to the transformation $\phi \to -\phi$, where ϕ is the relative azimuthal angle of the two electrons. Thus, if we drop for simplicity the index $\Lambda = 0$, the following equation is to be solved

$$H\Psi = E\Psi \quad (24)$$

where, cf. (7), (17) and (B.3),

$$H = H_0 + H_1 + H_2 + H_3,$$
$$H_0 = -\tfrac{1}{2}(\Delta_{\mathbf{r}_1} + \Delta_{\mathbf{r}_2}) + V \equiv T_0 + V,$$
$$H_1 = -(m/8\mu)(\Delta_{\mathbf{r}_1} + \Delta_{\mathbf{r}_2} + 2\nabla_{\mathbf{r}_1}\nabla_{\mathbf{r}_2}),$$
$$H_2 = -(m/2\mu)\langle 0|\Delta_\mathbf{R}|0\rangle,$$
$$H_3 = -(m/2\mu_a)\langle 0|\nabla_\mathbf{R}(\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2})|0\rangle. \quad (25)$$

The trial wave functions will be expanded in the form

$$\Psi = \frac{1}{2\pi}\sum_{i,n} c_{i,n} g_i(\xi_1,\eta_1,\xi_2,\eta_2,\phi)h_n(R). \quad (26)$$

Since the electronic functions g_i may contain the interelectronic distance, e.g., in the form of the usual factor $2r_{12}/R$, we shall assume

$$g_i = \rho_{p_i}\bar{g}_i(\xi_1,\eta_1,\xi_2,\eta_2), \quad (27)$$

and the product $R^{p_i}\rho_{p_i}$ will be treated as an R-independent function of the electronic coordinates x_j', y_j', z_j' in a space-fixed reference system. Thus the following relations are valid:

$$\nabla_\mathbf{R} R^{p_i}\rho_{p_i} = 0, \quad (28)$$

$$\int \Psi\Delta_\mathbf{R}\Psi d\tau_1 d\tau_2 d^3R$$
$$= \sum_{i,n} c_{in}\int \Psi R^{p_i}\rho_{p_i}\Delta_\mathbf{R} R^{-p_i}\bar{g}_i h_n\, d\tau_1 d\tau_2 d^3R. \quad (29)$$

All g_i functions in the expansion (26) have obviously the same symmetry with respect to the permutation of the two electrons, so that Ψ represents either a singlet or a triplet. Since we do not want to restrict our analysis to the homonuclear case we shall only assume that each of the component functions g_i has a definite symmetry with respect to the permutation of the nuclei, but no restriction is imposed on the symmetry of the total wave function with respect to this transformation.

To solve the variational problem

$$\delta\int \Psi H\Psi d\tau_1 d\tau_2 d^3R = 0, \quad (30)$$

with H and Ψ given by (25) and (26), respectively,

[10] Obviously it is also invariant under the electronic inversion I_e, however, I_e is dependent on I and I_n: $I_e = I \cdot I_n$.

[11] The constant value of $\Omega^0_{0,0}$ being dropped.

we have to evaluate the matrix elements

$$H_{ik}^{nm} = \int g_i h_n H g_k h_m d\tau_1 d\tau_2 d^3R \,,$$

$$S_{ik}^{nm} = \int g_i h_n g_k h_m d\tau_1 d\tau_2 d^3R \,. \tag{31}$$

Let us introduce the following notation

$$T'_{ik} = R^{-4}\int g_i T_0 g_k d\tau_1 d\tau_2 \,,$$

$$P'_{ik} = -R^{-4}\int g_i \nabla_{\mathbf{r}_1}\nabla_{\mathbf{r}_2} g_k d\tau_1 d\tau_2 \,, \tag{32}$$

$$V'_{ik} = R^{-5}\int g_i V g_k d\tau_1 d\tau_2 \,,$$

$$S'_{ik} = R^{-6}\int g_i g_k d\tau_1 d\tau_2 \,,$$

so that the dashed quantities are R independent. Then we get immediately

$$\frac{1}{4\pi}(H_0)_{ik}^{nm} = T'_{ik}K_{nm}^0 + V'_{ik}K_{nm}^1 \,,$$

$$\frac{1}{4\pi}(H_1)_{ik}^{nm} = \frac{m}{4\mu}(T'_{ik} + P'_{ik})K_{nm}^0 \,, \tag{33}$$

$$S_{ik}^{nm} = S'_{ik}K_{nm}^2 \,,$$

where

$$K_{nm}^s = \int_0^\infty R^{s+6} h_n h_m dR \,. \tag{34}$$

On applying (29) and (B.4) we also obtain

$$(H_2)_{ik}^{nm} = -\frac{2\pi m}{\mu}\Big\{S'_{ik}\int R^{8+P_k} h_n\Big(\frac{d^2}{dR^2} + \frac{2}{R}\frac{d}{dR}\Big) \times R^{-P_k} h_m dR - 4Y_{ik}\int R^{7+P_k} h_n \frac{d}{dR} R^{-P_k} h_m dR + (2B_{ik} + 2\overline{Y}_{ik} - 4Y_{ik} + 2X_{ik}) \times \int R^6 h_n h_m dR\Big\} \,, \tag{35}$$

where

$$X_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i(\xi_1^2 + \eta_1^2 - 1)X_1\bar{g}_k d\tau_1 d\tau_2 \,,$$

$$Y_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i Y_1 \bar{g}_k d\tau_1 d\tau_2 \,,$$

$$\overline{Y}_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i Y_1 Y_2 \bar{g}_k d\tau_1 d\tau_2 \,,$$

$$B_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i \cos\phi B_1 B_2 \bar{g}_k d\tau_1 d\tau_2 \,, \tag{36}$$

and the operators X_i, Y_i, and B_i are defined in the Appendix B.

The integration over R in (35) can readily be reduced to evaluation of K_{nm}^0 defined by (34), and of

$$L_{nm} = \tfrac{1}{2}\int R^7(h_n h'_m - h'_n h_m)dR \,,$$

$$N_{nm} = \tfrac{1}{2}\int R^8(h_n h''_m + h''_n h_m)dR \,, \tag{37}$$

where

$$h' = dh/dR \,, \quad h'' = d^2h/dR^2 \,.$$

Since the integrals K_{nm}^0 and N_{nm} are symmetric and L_{nm} antisymmetric in the indices n, m, and H_2 is a Hermitian operator we can get, after some manipulations, the final result in the following form:

$$(H_2)_{ik}^{nm} = -\frac{2\pi m}{\mu}\{S'_{ik}N_{nm} - [(p_k - p_i)S'_{ik} + 2(Y_{ik} - Y_{ki})]L_{nm} + [X_{ik} + X_{ki} + \overline{Y}_{ik} + \overline{Y}_{ki} + B_{ik} + B_{ki} + 2(p_k Y_{ik} + p_i Y_{ki}) + 5(Y_{ik} + Y_{ki}) + \tfrac{1}{2}(p_k^2 + p_i^2 + 6p_k + 6p_i - 14)S'_{ik}]K_{nm}\} \,. \tag{38}$$

A similar evaluation of $(H_3)_{ik}^{nm}$ is possible if we assume that $R^p\rho_p$ is only a function of the relative position of the two electrons. Then

$$(\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2})R^p\rho_p = 0 \,, \quad \nabla_{\mathbf{R}}R^p\rho_p = 0 \,, \tag{39}$$

and we get

$$(H_3)_{ik}^{nm} = -\frac{4\pi m}{u_a}\{(Z_{ik} - Z_{ki})L_{nm} - [\tfrac{1}{2}(p_k - p_i)(Z_{ik} - Z_{ki}) + \overline{X}_{ik} + \overline{X}_{ki} + (ZY)_{ik} + (ZY)_{ki} + (AB)_{ik} + (AB)_{ki}]K_{nm}\} \,, \tag{40}$$

where

$$Z_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i Z_1 \bar{g}_k d\tau_1 d\tau_2 \,,$$

$$\overline{X}_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i \xi_1\eta_1 X_1 \bar{g}_k d\tau_1 d\tau_2 \,,$$

$$(ZY)_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i Z_1 Y_2 \bar{g}_k d\tau_1 d\tau_2 \,,$$

$$(AB)_{ik} = R^{-6}\int \rho_{Pi}\rho_{Pk}\bar{g}_i \cos\phi A_1 B_2 \bar{g}_k d\tau_1 d\tau_2 \,. \tag{41}$$

It is clear that the matrix elements of H_3 do not vanish only if the functions g_i, g_k have different symmetries with respect to the permutation of the nuclei, whereas the remaining terms of the Hamiltonian contribute only if the symmetries of g_i and g_k are the same.

The vibrational functions were assumed in the form

$$h_n(R) = R^{-3} \exp\left[-\frac{\beta^2}{2}|R - R_e|^2\right]\mathcal{H}_n(\beta|R - R_e|) , \tag{42}$$

where β and R_e are variation parameters, and $\mathcal{H}_n$ denotes the nth Hermite polynomial. The R^{-3} factor in (42) cancels R^3 in the electronic volume element.

If the functions (42) are employed, the K^s_{nm}, L_{nm} and N_{nm} integrals, (34) and (37), can readily be expressed in terms of F^s_{nm},

$$F^s_{nm} = \int_{-\beta R_e}^{\infty} x^s e^{-x^2}\mathcal{H}_n(x)\mathcal{H}_m(x)dx ,$$

and since the well-known recurrence formula for the Hermite polynomials gives

$$F^s_{nm} = mF^{s-1}_{n,m-1} + \tfrac{1}{2} F^{s-1}_{n,m+1} ,$$

all integrals over R can be expressed in terms of F^0_{nm}. The evaluation is straightforward and elementary and will not be given here. The evaluation of F^0_{nm} is also simple. We have

$$F^0_{nm} = \int_{-a}^{\infty} e^{-x^2}\mathcal{H}_n(x)\mathcal{H}_m(x)dx$$

where $a = \beta R_e$. Applying the definition of the Hermite polynomials one gets

$$F^0_{nm} = (-1)^n \int_{-a}^{\infty} \mathcal{H}_m(x) \frac{d^n}{dx^n} e^{-x^2}dx . \tag{43}$$

Integrating (43) by parts, and applying the recurrence relation

$$\frac{d}{dx}\mathcal{H}_n(x) = 2n\mathcal{H}_{n-1}(x)$$

the following result is obtained:

$$F^0_{nm} = m!e^{-a^2} \sum_{k=0}^{m} \frac{2^k}{(m-k)!}\mathcal{H}_{m-k}(-a)\mathcal{H}_{n-k-1}(-a) \qquad n > m ,$$

$$F^0_{mm} = m!e^{-a^2} \sum_{k=0}^{m-1} \frac{2^k}{(m-k)!}\mathcal{H}_{m-k}(-a)\mathcal{H}_{m-k-1}(-a) + 2^m m! \int_{-a}^{\infty} e^{-x^2}dx . \tag{44}$$

Since for the hydrogen molecule the optimum value of a turns out to be about $a = 6.0$, the probability integral in (44) can be replaced by $\pi^{\frac{1}{2}}$ without losing accuracy.

5. NUMERICAL RESULTS AND DISCUSSION

Numerical computation for the ground state of the hydrogen molecule was carried out using the wave function (26) with vibrational functions, h_n, given by (42). The electronic functions g_i were assumed in the form

$$g_i = \exp[-\alpha(\xi_1 + \xi_2)]\{\xi_1^{p_i}\eta_1^{q_i}\xi_2^{r_i}\eta_2^{s_i} + \xi_1^{r_i}\eta_1^{s_i}\xi_2^{p_i}\eta_2^{q_i}\} \times \left(\frac{2r_{12}}{R}\right)^{m_i} . \tag{45}$$

Using (45) in (26) and putting $h_n =$ const, one gets the well-known expansion of the electronic wave function in elliptic coordinates.[12] The exponent α in this expansion is known to be a function of the internuclear distance R. However, for simplicity, we have treated α as an R independent variation parameter with a constant value for the whole range of the zero-point vibrations.

The method of computation of the integrals over R has been given at the end of the preceding section. All integrals over the electronic coordinates can be expressed in terms of the following integrals:

$$I_{pq\bar{p}\bar{q}}{}^m = \int \exp[-2\alpha(\xi_1 + \xi_2)](\xi_1^2 - \eta_1^2)^{-1}(\xi_2^2 - \eta_2^2)^{-1} \times \xi_1^p\eta_1^q\xi_2^{\bar{p}}\eta_2^{\bar{q}}r_{12}^m d\tau_1 d\tau_2 ,$$

which can be computed using the method given by Kołos and Roothaan.[13]

The computation was carried out on the IBM 704 computer at Argonne National Laboratory, using an eighty-term wave function (26). The wave function was built up of 40 different electronic terms (45) and of 4 $h_n(R)$ functions ($0 \leqslant n \leqslant 3$). The 40 electronic terms were the same as those used by Kołos and Roothaan[3] in their computation of the ground state potential energy curve for H_2. All 40 terms were coupled with h_0, a selected set of 18 terms with h_1, 16 with h_2 and 6 with h_3. The selection was made after some test runs in which, for given values of the nonlinear parameters, we gradually increased the length of the expansion. No energy depression was obtained by adding terms containing h_4. The energy has not been accurately minimized with respect to the nonlinear parameters α, β, R_e.

In Table I we show the results obtained with $\alpha = 0.95$, $\beta R_e = 6.0$ and $R_e = 1.4$. In addition to the dissociation energy D_0, we have computed the expectation value of the internuclear distance, and the

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[12] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[13] W. Kołos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 205 (1960).

inverse square root of the expectation value of $1/R^2$. The latter can be compared with the experimental value[14] obtained from the rotational constant B_0 for the zeroth vibrational level. It should be pointed out, however, that the experimental value of B_0 is not quite the same as the theoretical one computed in the present work. The experimental B_0 is obtained by measuring several rotational lines and by calculating, from these results, the coefficients in the energy formula for a vibrating rotator. Obviously, the theoretical evaluation of B_0 should be performed similarly, i.e., from the theoretical values of the rotational energy levels. However, up to terms of the relative order of m/μ, $\langle R^{-2}\rangle m/2\mu$ is a good approximation for B_0, which can be shown by the perturbation method. For this purpose, let us separate the exact Hamiltonian into two parts

TABLE I. Dissociation energy, expectation value of the internuclear distance and the inverse square root of the expectation value of R^{-2} for the ground state of the H_2 molecule.

	$D_0(\text{cm}^{-1})$	$\langle R\rangle$(a.u.)	$R_0 = \langle R^{-2}\rangle^{-\frac{1}{2}}$(a.u.)
theoretical	36 091	1.4481	1.4191
experimental	36 113		1.4193

$$H = \overline{H}_0 + \overline{H}' ,$$

where $\overline{H}_0$ is the diagonal part of H,

$$\langle \Lambda' | \overline{H}_0 | \Lambda \rangle = H_{\Lambda\Lambda}\delta_{\Lambda'\Lambda} ,$$

with $H_{\Lambda\Lambda}$ defined by (17). Now, after neglecting $\overline{H}'$, we get the Schrödinger equation

$$\overline{H}_0\Psi = E_0^0\Psi . \quad (46)$$

The solution of (46) obviously has the form

$$\Psi^K_{M_K,\Lambda} = \overline{u}_\Lambda^K \Omega^K_{M_K,\Lambda}(\theta,\varphi,\psi) \quad (47)$$

and $\overline{u}^K$ satisfies the equation

$$(H_{\Lambda\Lambda} - E^0_{K,\Lambda})\overline{u}_\Lambda^K = 0 . \quad (48)$$

In (48) we can treat $(m/2\mu)[K(K+1)/R^2]$ as a perturbation, and find $E^0_{K,\Lambda}$ in the form of the expansion

$$E^0_{K,\Lambda} = E^0_{0,\Lambda} + B_{0,\Lambda}K(K+1) + D_{0,\Lambda}K^2(K+1)^2 + \cdots ,$$

where

$$B_{0,\Lambda} = \frac{m}{2\mu}\int R^{-2}|\overline{u}_\Lambda^0|^2 d\tau d^3R$$

and $\overline{u}_\Lambda^0$ is the solution of (48) with $K = 0$, corresponding to the lowest eigenvalue $E^0_{0,\Lambda}$.

It is easily seen from (17) and (48) that in the case of a $\sum$ state (i.e., $\Lambda = 0$) $\overline{u}_0^0$ is identical with the solution of the exact Schrödinger Eq. (18), and we have

$$B_0 \cong B_{0,0} = \langle R^{-2}\rangle m/2\mu , \quad (49)$$

where $\langle R^{-2}\rangle$ means the mean value computed with the exact ground-state wave function.

In a similar way it can be shown that if the correction to $B_{0,0}$, due to the nondiagonal part of the Hamiltonian is computed, one gets

$$B_0 = B_{0,0}(1 - \Delta) , \quad (50)$$

where Δ is positive and of the order of m/μ. Now from (50) and (49) it is seen that the relation between the theoretical and experimental values of R_0 is

$$(R_0)_{\text{th}} = (R_0)_{\text{expt}}(1 - \Delta)^{\frac{1}{2}} .$$

Thus, the error in the theoretical value of R_0, shown in Table I, has the correct order of magnitude and the correct sign.

The discrepancy between the theoretical and experimental value of the dissociation energy, which amounts to 22 cm^{-1}, can be attributed to the following factors, which are listed in the probable order of decreasing importance: (a) nonoptimum values of the nonlinear parameters; (b) R independence of the electronic exponent α; (c) truncation of the expansion; (d) relativistic effects. The factors (b) and (c) are obviously interrelated, since in the case of a complete set the value of α becomes immaterial. It may be pointed out that the expectation value of R differs significantly, as expected, from the so called equilibrium internuclear distance $R_e = 1.4014$ a.u.

It should be also pointed out that in the method applied in this work all integrations over the internuclear distance can readily be performed and the computation is practically not more laborious than the computation of the correction C_{nn} in Eq. (6), in spite of the fact that our approach gives the complete electronic–vibrational wave function.

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[14] G. Herzberg and L. L. Howe, Can. J. Phys. **37**, 636 (1959).

APPENDIX A

The functions $\vartheta^K_{M_K\Lambda}$ fulfill the following relations which are useful in the evaluation of the matrix elements (17):

$$\left\{\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+2M_K\Lambda\frac{\cot\theta}{\sin\theta}-\frac{M_K^2+\Lambda^2}{\sin^2\theta}+K(K+1)\right\}\vartheta^K_{M_K,\Lambda}=0\,, \tag{A.1}$$

$$\left(\frac{\partial}{\partial\theta}-\Lambda\cot\theta+\frac{M_K}{\sin\theta}\right)\vartheta^K_{M_K,\Lambda}=[(K+\Lambda+1)(K-\Lambda)]^{\frac12}\vartheta^K_{M_K,\Lambda+1}\,, \tag{A.2}$$

$$\left(-\frac{\partial}{\partial\theta}-\Lambda\cot\theta+\frac{M_K}{\sin\theta}\right)\vartheta^K_{M_K,\Lambda}=[(K+\Lambda)(K-\Lambda+1)]^{\frac12}\vartheta^K_{M_K,\Lambda-1}\,, \tag{A.3}$$

$$\vartheta^K_{M_K,\Lambda}(\theta)=\frac{1}{2^K}\left[\frac{(2K+1)(K+M_K)!}{2(K-\Lambda)!(K+\Lambda)!(K-M_K)!}\right]^{\frac12}\times\frac{(1-x)^{\frac12(\Lambda-M_K)}}{(1+x)^{\frac12(\Lambda+M_K)}}\left(\frac{d}{dx}\right)^{K-M_K}(1-x)^{K-\Lambda}\times(1+x)^{K+\Lambda}\,, \tag{A.4}$$

where $x=\cos\theta$,

$$\vartheta^K_{M_K,\Lambda}(\pi-\theta)=(-1)^{K-M_K}\vartheta^K_{M_K,-\Lambda}(\theta)\,. \tag{A.5}$$

These, and other similar relations have been given by Gelfand *et al.*[15] It is to be noticed however, that our $\vartheta^K_{M_K\Lambda}(\theta)$ differs from the functions $u^K_{M_K\Lambda}(\theta)$ used by Gelfand *et al.* by a factor:

$$\vartheta^K_{M_K,\Lambda}(\theta)=(-1)^K i^{-(M_K+\Lambda)}\left[\tfrac12(2K+1)\right]^{\frac12}u^K_{M_K,\Lambda}(\theta)\,.$$

APPENDIX B

The explicit form of the operators occuring in (17), in the case of a two-electron molecule, will now be given. For this purpose we shall use the internal coordinates (19):

$$R,\xi_1,\eta_1,\xi_2,\eta_2,\phi\,,\qquad \phi\equiv\phi_1\,.$$

To abbreviate the notation let us introduce the operators:

$$A_i=\frac{[(\xi_i^2-1)(1-\eta_i^2)]^{\frac12}}{\xi_i^2-\eta_i^2}\left(\xi_i\frac{\partial}{\partial\xi_i}-\eta_i\frac{\partial}{\partial\eta_i}\right),$$

$$B_i=\frac{[(\xi_i^2-1)(1-\eta_i^2)]^{\frac12}}{\xi_i^2-\eta_i^2}\left(\eta_i\frac{\partial}{\partial\xi_i}-\xi_i\frac{\partial}{\partial\eta_i}\right),$$

$$X_i=(\xi_i^2-\eta_i^2)^{-1}\left\{\frac{\partial}{\partial\xi_i}(\xi_i^2-1)\frac{\partial}{\partial\xi_i}+\frac{\partial}{\partial\eta_i}(1-\eta_i^2)\frac{\partial}{\partial\eta_i}\right\},$$

$$Y_i=(\xi_i^2-\eta_i^2)^{-1}\left\{\xi_i(\xi_i^2-1)\frac{\partial}{\partial\xi_i}+\eta_i(1-\eta_i^2)\frac{\partial}{\partial\eta_i}\right\},$$

$$Z_i=(\xi_i^2-\eta_i^2)^{-1}\left\{\eta_i(\xi_i^2-1)\frac{\partial}{\partial\xi_i}+\xi_i(1-\eta_i^2)\frac{\partial}{\partial\eta_i}\right\}.$$

After some elementary manipulations one gets in this notation the matrix elements in the form[16]:

$$\langle\Lambda+1|L^+|\Lambda\rangle=e^{(i/2)\phi}\left\{B_1-\frac{\xi_1\eta_1}{[(\xi_1^2-1)(1-\eta_1^2)]^{\frac12}}\times\left(\frac{\Lambda}{2}-i\frac{\partial}{\partial\phi}\right)\right\}+e^{-(i/2)\phi}\left\{B_2-\frac{\xi_2\eta_2}{[(\xi_2^2-1)(1-\eta_2^2)]^{\frac12}}\times\left(\frac{\Lambda}{2}+i\frac{\partial}{\partial\phi}\right)\right\},$$

$$\langle\Lambda-1|L^-|\Lambda\rangle=-e^{-(i/2)\phi}\left\{B_1+\frac{\xi_1\eta_1}{[(\xi_1^2-1)(1-\eta_1^2)]^{\frac12}}\times\left(\frac{\Lambda}{2}-i\frac{\partial}{\partial\phi}\right)\right\}-e^{(i/2)\phi}\left\{B_2+\frac{\xi_2\eta_2}{[(\xi_2^2-1)(1-\eta_2^2)]^{\frac12}}\times\left(\frac{\Lambda}{2}-i\frac{\partial}{\partial\phi}\right)\right\}, \tag{B.1}$$

$$\langle\Lambda+1|P^+|\Lambda\rangle=-\frac{2i}{R}\left\{e^{(i/2)\phi}\left[A_1+\frac{-\frac{\Lambda}{2}+i\frac{\partial}{\partial\phi}}{[(\xi_1^2-1)(1-\eta_1^2)]^{\frac12}}\right]+e^{-(i/2)\phi}\left[A_2-\frac{\frac{\Lambda}{2}+i\frac{\partial}{\partial\phi}}{[(\xi_2^2-1)(1-\eta_2^2)]^{\frac12}}\right]\right\},$$

$$\langle\Lambda-1|P^-|\Lambda\rangle=$$

[15] I. M. Gelfand, R. A. Minlos, and Z. Ya. Shapiro, *Predstavleniya grupi vrashchenii i grupi Lorentsa, ikh primeneniya* (Fizmatgiz, Moskva, 1958).

[16] For $K=0$ and $\Lambda=0$ (B.4) has been given by W. Kołos and L. Wolniewicz [Acta Phys. Polon. **20**, 129 (1961)]; however there are some misprints in those formulas.

$$-\frac{2i}{R}\left\{e^{-(i/2)\phi}\left[A_1+\frac{\frac{\Lambda}{2}-i\frac{\partial}{\partial\phi}}{[(\xi_1^2-1)(1-\eta_1)]^{\frac{1}{2}}}\right]+e^{(i/2)\phi}\left[A_2+\frac{\frac{\Lambda}{2}+i\frac{\partial}{\partial\phi}}{[(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}}\right]\right\}, \quad \text{(B.2)}$$

$$\langle\Lambda|\Delta_{\mathbf{r}_1}|\Lambda\rangle=\frac{4}{R^2}\left\{X_1+[(\xi_1^2-1)(1-\eta_1^2)]^{-1}\times\left(\frac{\partial^2}{\partial\phi^2}+i\Lambda\frac{\partial}{\partial\phi}-\frac{\Lambda^2}{4}\right)\right\},$$

$$\langle\Lambda|\Delta_{\mathbf{r}_2}|\Lambda\rangle=\frac{4}{R^2}\left\{X_2+[(\xi_2-1)(1-\eta_2^2)]^{-1}\times\left(\frac{\partial^2}{\partial\phi^2}-i\Lambda\frac{\partial}{\partial\phi}-\frac{\Lambda^2}{4}\right)\right\}, \quad \text{(B.3)}$$

$$\langle\Lambda|\Delta_{\mathbf{R}}|\Lambda\rangle=\frac{\partial^2}{\partial R^2}+\frac{2}{R}\frac{\partial}{\partial R}+\frac{1}{R^2}\left[-K(K+1)+\frac{3}{2}\Lambda^2-2\frac{\partial^2}{\partial\phi^2}\right]+\frac{2}{R^2}Y_1Y_2$$
$$-\frac{2}{R^2}(Y_1+Y_2)\left(1+R\frac{\partial}{\partial R}\right)$$
$$+\tfrac{1}{4}\{(\xi_1^2+\eta_1^2-1)\langle\Lambda|\Delta_{r_1}|\Lambda\rangle+(\xi_2^2+\eta_2^2-1)\langle\Lambda|\Delta_{r_2}|\Lambda\rangle\}+\frac{2}{R^2}\left\{\cos\phi\left[B_1B_2-\frac{\xi_1\eta_1\xi_2\eta_2}{[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}}\left(\frac{\Lambda^2}{4}+\frac{\partial^2}{\partial\phi^2}\right)\right]\right.$$
$$\left.+\sin\phi\left[\frac{\xi_1\eta_1B_2}{[(\xi_1^2-1)(1-\eta_1^2)]^{\frac{1}{2}}}\left(-\frac{i\Lambda}{2}-\frac{\partial}{\partial\phi}\right)+\frac{\xi_2\eta_2B_1}{[(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}}\left(\frac{i\Lambda}{2}-\frac{\partial}{\partial\phi}\right)\right]\right\}, \quad \text{(B.4)}$$

$$\langle\Lambda|\nabla_{\mathbf{R}}(\nabla_{\mathbf{r}_1}+\nabla_{\mathbf{r}_2})|\Lambda\rangle=\frac{2}{R^2}(Z_1+Z_2)\left(1+R\frac{\partial}{\partial R}\right)$$
$$-\frac{2}{R^2}(Z_1Y_2+Z_2Y_1)-\tfrac{1}{2}\{\xi_1\eta_1\langle\Lambda|\Delta_{r_1}|\Lambda\rangle+\xi_2\eta_2\langle\Lambda|\Delta_{r_2}|\Lambda\rangle\}-\frac{2\cos\phi}{R^2}\left\{A_1B_2+A_2B_1-\frac{\xi_1\eta_1+\xi_2\eta_2}{[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}}\left(\frac{\Lambda^2}{4}+\frac{\partial^2}{\partial\phi^2}\right)\right\}$$
$$-\frac{2\sin\phi}{R^2}\left\{\frac{B_1+\xi_2\eta_2A_1}{[(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}}\left(\frac{i\Lambda}{2}-\frac{\partial}{\partial\phi}\right)-\frac{B_2+\xi_1\eta_1A_2}{[(\xi_1^2-1)(1-\eta_1^2)]^{\frac{1}{2}}}\left(\frac{i\Lambda}{2}+\frac{\partial}{\partial\phi}\right)\right]\right\}, \quad \text{(B.5}$$

$$\langle\Lambda|\nabla_{\mathbf{r}_1}\nabla_{\mathbf{r}_2}|\Lambda\rangle=\frac{4}{R^2}\cos\phi A_1A_2-\frac{4\sin\phi}{R^2}\times\left\{\frac{A_2\left(\frac{\partial}{\partial\phi}+i\frac{\Lambda}{2}\right)}{[(\xi_1^2-1)(1-\eta_1^2)]^{\frac{1}{2}}}+\frac{A_1\left(\frac{\partial}{\partial\phi}-i\frac{\Lambda}{2}\right)}{[(\xi_2^2-1)(1-\eta_2^2)]^{\frac{1}{2}}}\right\}$$
$$-\frac{4}{R^2}[(\xi_1^2-1)(1-\eta_1^2)(\xi_2^2-1)(1-\eta_2^2)]^{-\frac{1}{2}}\times\left\{\cos\phi\left(\frac{\partial^2}{\partial\phi^2}+\frac{\Lambda^2}{4}\right)-\xi_1\eta_1\xi_2\eta_2A_1A_2-B_1B_2+\xi_1\eta_1A_1B_2+\xi_2\eta_2B_1A_2\right\}. \quad \text{(B.6)}$$

Since

$$\mathbf{P}^2=-\Delta_{\mathbf{r}1}-\Delta_{\mathbf{r}2}-2\nabla_{\mathbf{r}1}\nabla_{\mathbf{r}2}$$

the formulas (B.1)–(B.6) together with the relations (17) give the Hamiltonian in the angular-momentum representation.