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HAMILTONIAN FOR DIATOMIC MOLECULE

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The simplest diatomic molecule HD^+ consists of proton p with mass m_p, deuteron d with mass m_d, and electron e with mass m_e. As independent internal variables we choose a vector $\vec{R}$ connecting proton with deuteron and a vector $\vec{r}$ connecting the midpoint of the vector $\vec{R}$ and electron. Then, we introduce polar coordinates $\{R, \Theta, \Phi\}$ for the vector $\vec{R}$ and elliptical coordinates $\{\xi, \eta, \varphi\}$ for the vector $\vec{r}$

$$x = \frac{R}{2} S \cos\varphi, \quad y = \frac{R}{2} S \sin\varphi, \quad z = \frac{R}{2} \xi\eta;$$

$$S = \sqrt{(\xi^2-1)(1-\eta^2)} \quad (1 \le \xi < \infty, \; -1 \le \eta \le 1). \tag{1}$$

The variables ξ and η can simply be defined by distances from electron to nuclei $r_1 = r_{ep}$ and $r_2 = r_{ed}$

$$\xi = (r_1 + r_2)/R, \quad \eta = (r_1 - r_2)/R. \tag{1a}$$

An important point is that the unit vectors of the coordinate system for the vector $\vec{r}$ coincide with the spherical unit vectors of $\vec{R}$

$$\vec{e}_x = \vec{e}_\Theta, \quad \vec{e}_y = \vec{e}_\Phi, \quad \vec{e}_z = \vec{e}_R \tag{1b}$$

which are functions of Θ and Φ /1/.

The Hamiltonian of the problem in these variables is of the conventional form

$$H = -\frac{1}{2m}\Delta_r + V - \frac{1}{2MR^2}\left(\vec{r} + \frac{\varkappa\vec{R}}{2}\right)^2 \Delta_r \tag{2}$$
$$- \frac{1}{2M}\left(\frac{1}{R} + \frac{\partial}{\partial R}\right)^2 + \frac{1}{MR}\left(\frac{1}{R} + \frac{\partial}{\partial R}\right)\hat{q} + \frac{\vec{K}^2 - 2\vec{K}\cdot\vec{\ell}}{2MR^2},$$

where the following notation is used:

$$\hat{q} = r\frac{\partial}{\partial r} + \frac{\varkappa R}{2}\frac{\partial}{\partial z} \tag{2a}$$
$$\frac{1}{m} = \frac{1}{m_e} + \frac{1}{m_p + m_d}, \quad \frac{1}{M} = \frac{1}{m_p} + \frac{1}{m_d}, \quad \varkappa = \frac{m_d - m_p}{m_d + m_p}.$$

The operator of the total orbital momentum of the system $\vec{K}$ and orbital momentum of electron $\vec{\ell}$ are given in the unit vectors $\vec{e}_\Theta$, $\vec{e}_\Phi$, and $\vec{e}_R$, in particular

$$\vec{K} = \vec{e}_\Theta\left(\frac{i}{\sin\Theta}\frac{\partial}{\partial\Phi} - i\frac{\partial}{\partial\varphi}\right) + \vec{e}_\Phi\left(-i\frac{\partial}{\partial\Theta}\right) + \vec{e}_R\left(-i\frac{\partial}{\partial\varphi}\right). \tag{3}$$

The potential energy of the problem has the form

$$V = -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R} \tag{2b}$$

and the volume element is expressed by

$$d\tau = \frac{R^5}{8} dR\,(\xi^2 - \eta^2)\,d\xi\,d\eta\,d\varphi\,d(\cos\Theta)\,d\Phi. \tag{2c}$$

All the operators entering into Hamiltonian (2) should be given through the variables $\{R, \Theta, \Phi, \xi, \eta, \varphi\}$ (see, for instance, papers /2,3/).

The corresponding Shrödinger equation

$$H\Psi(\vec{R}, \vec{r}) = E\Psi(\vec{R}, \vec{r}) \tag{4}$$

is a usual starting point in the theory of diatomic molecule /4/. Of common use is also the following way of its solution. The Hamiltonian is splitted into the "electron"

$$h = -\frac{1}{2m}\Delta_r + V \tag{5}$$

and "nuclear" part. Next, the electron problem

$$h\varphi(\vec{r}; R) = \varepsilon(R)\varphi(\vec{r}; R) \tag{5a}$$

is solved, the eigenvalues and eigenfunctions of which depend on R parametrically. Finally, the vibronic spectrum of the molecule is found from the equation

$$\left[-\frac{1}{2M}\left(\frac{1}{R} + \frac{\partial}{\partial R}\right)^2 + \varepsilon(R)\right]\chi_v(R) = E_v\chi_v(R). \tag{6}$$

In this approximation the wave function of eq. (4) is of a simple form

$$\Psi(\vec{R}, \vec{r}) = \varphi(\vec{r}; R)\chi_v(R). \tag{7}$$

In the rigorous approach the solution of the problem should be expanded over the total set of eigenfunctions of problem (5a) /3/. In this case each operator of Hamiltonian (2) generates matrix elements, and eq. (6) turns into the system of Shrödinger equations.

The matrix elements forming this system of equations tend to constant values as $R \to \infty$ (infinite separation of nuclei). This is well demonstrated by numerous pictures of matrix elements from review [3]. This asymptotic effect is caused by that the total Hamiltonian (2) does not disintegrate into the sum of subsystem Hamiltonians as $R \to \infty$ in contrast with the physical situation. In particular, the approximate wave function (7) does not provide an exact dissociation limit for the molecule, that immediately follows from the form of the electron Hamiltonian (5).

This paper is aimed at constructing of an asymptotically correct Hamiltonian for the diatomic molecule.

In paper [5] the generalized variable

$$\rho = 1 + \frac{m}{MR^2}\left(\vec{z} + \frac{\varkappa \vec{R}}{2}\right)^2 \tag{8}$$

has first been introduced, and after that in paper [2] the generator

$$\Lambda = \ln(\sqrt{\rho})\left(1 + R\frac{\partial}{\partial R}\right) \tag{9}$$

has been found in order to perform a "canonical" transformation of Hamiltonian as follows:

$$H_\Lambda = e^{-\Lambda} H e^{\Lambda} = H - [\Lambda, H] + \frac{1}{2!}[\Lambda,[\Lambda,H]] + \ldots \tag{10}$$

The transformed Hamiltonian H_Λ happened to have a simple form [2]

$$H_\Lambda = \rho\Big[-\frac{1}{2m/\rho}\Delta_z + \frac{V}{\sqrt{\rho}} - \frac{1}{2M\rho}\left(\frac{\partial^2}{\partial R^2} + \frac{5}{R}\frac{\partial}{\partial R}\right) - \frac{3}{2}\frac{1}{M\rho R^2} + \frac{\vec{K}^2 - 2\vec{K}\cdot\vec{\ell}}{2MR^2}\Big] \tag{11}$$

since it does not contain the cross derivative term $\left(\frac{1}{R} + \frac{\partial}{\partial R}\right)\left(z\frac{\partial}{\partial z} + \frac{\varkappa R}{2}\frac{\partial}{\partial z}\right)$ generating matrix elements with unphysical asymptotic behaviour. However, the generator Λ commutes with the operator $\vec{K}\cdot\vec{\ell}$ leaving it unchanged, but, unfortunately, with the same unsatisfactory asymptotic properties.

Now we make a transformation which will improve the asymptotic properties of H_Λ. To this end, we introduce the generalized variable

$$\omega = 2\frac{m}{MR^2}\frac{\left(z + \frac{\varkappa R}{2}\right)\sqrt{x^2 + y^2}}{\rho} \tag{12}$$

and form the generator

$$\Omega = -i\frac{\omega}{2}K_1 \tag{12a}$$

with

$$K_1 = i\frac{\sin\varphi}{\sin\theta}\left(\frac{\partial}{\partial\Phi} - \cos\theta\frac{\partial}{\partial\varphi}\right) + i\cos\varphi\frac{\partial}{\partial\theta} \tag{13}$$

being the projection of the vector of the total orbital momentum $\vec{K}$ onto the axis perpendicular to the plane involving all three particles: proton, deuteron, and electron. We now define the new Hamiltonian by the "canonical" transformation

$$H_{\Lambda\Omega} = e^{-\Omega} H_\Lambda e^{\Omega} = H_\Lambda - [\Omega, H_\Lambda] + \frac{1}{2!}[\Omega,[\Omega,H_\Lambda]] + \ldots \tag{14}$$

Series (14) is exactly summed, but here we keep only the terms up to an order of $(m/M)^2$

$$H_{\Lambda\Omega} = \rho\Big[-\frac{1}{2m/\rho}\Delta_z + \frac{V}{\sqrt{\rho}} - \frac{1}{2M\rho}\left(\frac{\partial^2}{\partial R^2} + \frac{5}{R}\frac{\partial}{\partial R}\right) - \frac{3}{2}\frac{1}{M\rho R^2} + \frac{\vec{K}^2 - 2\ell_z^2}{2M\rho R^2} + \frac{iK_1}{MR^2}\Big\{(2\mathcal{L}_1 - \omega) - \omega\left(\mathcal{L}_2 + \frac{2}{\rho} + \frac{1}{2}\right)\Big\}\Big]. \tag{15}$$

In this expression $\mathcal{L}_1$ and $\mathcal{L}_2$ are the differential operators

$$\mathcal{L}_1 = \sqrt{x^2 + y^2}\frac{\partial}{\partial z}, \quad \mathcal{L}_2 = \hat{q} \tag{15a}$$

$$\mathcal{L}_2 \cancel{= \frac{4}{R^2}\left(z + \frac{\varkappa R}{2}\right)}\sqrt{x^2 + y^2}\,\hat{q}.$$

Hamiltonian (14) is the Hermitian operator with the volume element

$$d\tau_{\Lambda\Omega} = d\tau/\rho^2 \tag{15b}$$

and has a remarkable asymptotic behaviour

$$H_{\Lambda\Omega} \xrightarrow[R\to\infty]{} \rho\Big[-\frac{1}{2m/\rho}\Delta_z + \frac{V}{\sqrt{\rho}} - \frac{1}{2M\rho}\left(\frac{\partial^2}{\partial R^2} + \frac{5}{R}\frac{\partial}{\partial R}\right) - \frac{3}{2M\rho R^2} + \frac{\vec{K}^2 - 2\ell_z^2}{2\rho MR^2}\Big]. \tag{15'}$$

It follows from this expression that the Hamiltonian $H_{\Lambda\Omega}$ in the limit of infinitely separated nuclei provides an exact dissociation limit of the molecule even in the one-state approximation of type (7), since its electronic part

$$h_\rho = -\frac{\rho^2}{2m}\Delta_z + \sqrt{\rho}\,V \tag{16}$$

turns into the Hamiltonian of atom H or D taking exactly into account the isotopic effect as $R \to \infty$ [2].

In conclusion, let us discuss the Hamiltonian $H_{\Lambda\Omega}$ as compared to the results of paper [6], in which an attempt has been made to take the isotopic effect into account within the traditional approach. The authors of that paper derived a cumbersome expression for vibronic and rotational mass. A formal use of such parameters allows one to reach a better agreement between experiment and theory in the case of the molecular H_2 spectrum. It follows directly from formula (15) that the vibrational mass coincides with the rotational one up to terms $(m/M)^2$ and should be ρM. This conclusion does not contradict the results of paper [6]. The discussion of the results of review [3] can be carried out along the same line.

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Матвеенко А.В. E4-84-518
Гамильтониан для двухатомной молекулы

Построено преобразование гамильтониана простейшей двухатомной молекулы, которое упрощает его вид при бесконечном удалении одного из ядер, обеспечивая точный предел диссоциации молекулы.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Hamiltonian for Diatomic Molecule

The transformation of the diatomic Hamiltonian is proposed which simplifies its form and makes it asymptotically correct.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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