

# Hamiltonian for a diatomic molecule

A. V. Matveenko

*Joint Institute for Nuclear Research*

(Submitted 3 August 1984; resubmitted 24 October 1984)

Pis'ma Zh. Eksp. Teor. Fiz. **40**, No. 11, 493–495 (10 December 1984)

The first asymptotically correct Hamiltonian is derived for a diatomic molecule. The effectiveness of this Hamiltonian is demonstrated by using the “molecule”  $eee^+$  as an example.

The Hamiltonian that has been used to calculate the spectrum of a diatomic molecule<sup>1</sup> has poor asymptotic properties. As one of the nuclei is withdrawn to infinity, all the nonadiabatic corrections to the primary, adiabatic, part of the Hamiltonian are conserved. A coupling remains between the electronic and nuclear motion, as does a coupling between the rotation and the vibration of the molecule. In particular, the theory does not accurately predict the dissociation limit of the molecule.

An attempt was made in Refs. 2 and 3 to derive an effective vibrational-rotational Hamiltonian by projecting the nonadiabatic interactions onto the electronic ground state. Here it is first necessary to find a large number of electronic states and to calculate the corresponding matrix elements.<sup>3</sup>

In the present letter we transform the Hamiltonian in a way that completely eliminates the nonadiabatic effects when one of the nuclei is removed to infinity and

partially eliminates them in the region of finite nuclear separations. Formally, this new Hamiltonian describes the motion of quasiparticles with masses and charges that are functions of the relative coordinates of the particles.

We consider the simple molecule  $\text{HD}^+$ , consisting of a proton of mass  $m_p$ , a deuteron of mass  $m_d$ , and an electron of mass  $m_e$ . In the center-of-mass coordinate system, we choose as the independent variables the vector ( $\mathbf{R}$ ) that connects the proton with the deuteron and the vector ( $\mathbf{r}$ ) that connects the center of the vector  $\mathbf{R}$  with the electron. We then introduce polar coordinates  $\{R, \Theta, \Phi\}$  for the vector  $\mathbf{R}$  and elliptical coordinates  $\{\xi, \eta, \varphi\}$  for the vector  $\mathbf{r}(x, y, z)$ :

$$x = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \cos \varphi, \quad y = \frac{R}{2} \sqrt{(\xi^2 - 1)(1 - \eta^2)} \sin \varphi,$$

$$z = \frac{R}{2} \xi \eta (1 \leq \xi < \infty, -1 \leq \eta \leq 1).$$

The variables  $\xi$  and  $\eta$  can be expressed in a simple way in terms of the distances from the electron to the nuclei,  $r_1 = r_{ep}$  and  $r_2 = r_{ed}$ ;  $\xi = (r_1 + r_2)/R$ ,  $\eta = (r_1 - r_2)/R$ .

In terms of these variables, the Hamiltonian of the problem becomes

$$H = -\frac{1}{2m} \Delta_r + V - \frac{1}{2M} \left( \frac{1}{R} + \frac{1}{\partial R} \right)^2 + \frac{1}{MR} \left( \frac{1}{R} + \frac{\partial}{\partial R} \right) \hat{q} + \frac{\mathbf{K}^2 - 2\mathbf{Kl}}{2MR^2} - \frac{(r + \kappa R)^2}{2MR^2} \Delta_r. \quad (1)$$

where

$$\frac{1}{m} = \frac{1}{m_e} + \frac{1}{m_p + m_d}, \quad \frac{1}{M} = \frac{1}{m_p} + \frac{1}{m_d}, \quad \kappa = \frac{m_d - m_p}{m_d + m_p}, \quad (2)$$

and the operators  $\mathbf{K}$  and  $\mathbf{l}$  represent the total angular momentum of the system and the angular momentum of the electron, respectively. The operator  $\mathbf{K}$  is specified in terms of the spherical unit vectors  $\mathbf{e}_\Theta = \mathbf{e}_x$ ,  $\mathbf{e}_\Phi = \mathbf{e}_y$ ,  $\mathbf{e}_R = \mathbf{e}_z$  as follows:

$$\mathbf{K} = \mathbf{e}_\Theta \left( \frac{i}{\sin \Theta} \frac{1}{\partial \Phi} - i \frac{\partial}{\partial \varphi} \right) + \mathbf{e}_\Phi \left( -i \frac{\partial}{\partial \Theta} \right) + \mathbf{e}_R \left( -i \frac{\partial}{\partial \varphi} \right). \quad (3)$$

Furthermore, the operator  $\hat{q}$  and the potential energy  $V$  of the problem are

$$\hat{q} = r \frac{\partial}{\partial r} + \frac{\kappa R}{r} \frac{\partial}{\partial z}; \quad V = -\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}. \quad (3a)$$

All the operators in Hamiltonian (1) must be written in terms of the variables  $\{R, \Theta, \Phi, \xi, \eta, \varphi\}$ , as is done in Refs. 3 and 4, among other places.

The Schrödinger equation with Hamiltonian (1),

$$H \Psi(\mathbf{R}, \mathbf{r}) = E \Psi(\mathbf{R}, \mathbf{r}), \quad (4)$$

is a standard equation in the theory of a diatomic molecule<sup>1</sup>:

$$\int \Psi_i \Psi_j d\tau = \delta_{ij}, \quad d\tau = \frac{R^5}{8} (\xi^2 - \eta^2) dR d(\cos\Theta) d\Phi, d\xi d\eta d\varphi.$$

In the conventional approach to the solution of this equation, one first finds the ground state of the electronic problem,

$$h \varphi(\mathbf{r}; R) = \epsilon(R) \varphi(\mathbf{r}; R); \quad h = -\frac{1}{2m} \Delta_{\mathbf{r}} + V. \quad (5)$$

The vibrational spectrum of the molecule is then determined from the equation

$$\left[ -\frac{1}{2M} \left( \frac{1}{R} + \frac{\partial}{\partial R} \right)^2 + \epsilon(R) \right] \psi_v(R) = E_v \psi_v(R). \quad (6)$$

In this approximation the wave function takes the simple form

$$\Psi(\mathbf{R}; \mathbf{r}) = \varphi(\mathbf{r}; R) \psi_v(R). \quad (7)$$

In a rigorous approach,  $\Psi(\mathbf{R}, \mathbf{r})$  is sought as an expansion in the complete set of solutions of problem (5). The operators in Hamiltonian (2) then generate a system of Schrödinger equations. The matrix elements that form this system of equations tend toward nonvanishing limiting values in the limit  $R \rightarrow \infty$  (see the figures in the review by Vinitiskii and Ponomarev<sup>3</sup>). This means that there is no separation of variables even in the limit  $R \rightarrow \infty$ . In particular, Hamiltonian (5) does not accurately predict the dissociation limit of the molecule. We turn now to the construction of an asymptotically correct Hamiltonian.

We introduce the generalized variables  $\rho$  and  $\omega$  and the operators  $\Lambda$  (Ref. 4) and  $\Omega$ :

$$\rho = 1 + \frac{m}{MR^2} \left( \mathbf{r} + \frac{\kappa \mathbf{R}}{2} \right)^2, \quad \Lambda = \ln(\sqrt{\rho}) R \left( \frac{1}{R} + \frac{\partial}{\partial R} \right), \quad (8)$$

$$\omega = 2 \frac{m}{\rho MR^2} \left( z + \frac{\kappa R}{2} \right) \sqrt{x^2 + y^2}, \quad \Omega = -i \frac{\omega}{2} K_1.$$

Here  $K_1$  is the projection of the operator representing the total angular momentum,  $\mathbf{K}$ , onto an axis perpendicular to the plane containing the molecule. The Hamiltonian that we are seeking is defined by the transformation

$$H_{\Lambda\Omega} = \exp(-\Omega) \exp(-\Lambda) H \exp(\Lambda) \exp(\Omega), \quad (9)$$

which consists of sequential extensions along the coordinate  $R$  and a rotation in the plane of the molecule. The transformation parameters depend on the coordinates. The Hamiltonian  $H_{\Lambda\Omega}$  is calculated from

$$\exp(-\hat{a}) \hat{b} \exp(\hat{a}) \hat{b} - [\hat{a}, \hat{b}] + \frac{1}{2!} [\hat{a}, [\hat{a}, \hat{b}]] + \dots; \quad (9a)$$

the infinite series that arise here are summed in closed form. The Hamiltonian  $H_{\Lambda\Omega}$  is a self-adjoint operator on functions with a scalar product  $\int d\tau_{\Lambda\Omega} \Psi_i \Psi_j = \delta_{ij}$ ,  $d\tau_{\Lambda\Omega} = d\tau/\rho^2$ . It does not contain a radial-coupling operator  $(1/R + \partial/\partial R) \hat{q}$ , and it

has a remarkable asymptotic behavior:

$$H_{\Lambda\Omega} \xrightarrow{R \rightarrow \infty} \rho_a \left[ -\frac{1}{2m/\rho_a} \Delta_r + \frac{V}{\sqrt{\rho_a}} - \frac{1}{2M\rho_a} \left( \frac{\partial}{\partial R^2} + \frac{5}{R} \frac{\partial}{\partial R} \right) - \frac{3}{2M\rho_a R^2} + \frac{K^2 - 2I_z^2}{2M\rho_a R^2} \right], \quad (10)$$

Here  $\rho_a = \lim_{R \rightarrow \infty} \rho$  is a constant,<sup>4</sup> so that Hamiltonian (10) describes a system with separable variables. For infinite values of  $R$  it becomes

$$H_{\Lambda\Omega} = \rho \left[ -\frac{1}{2m/\rho} \Delta_r + \frac{V}{\sqrt{\rho}} - \frac{1}{2M\rho} \left( \frac{\partial}{\partial R^2} + \frac{5}{R} \frac{\partial}{\partial R} \right) - \frac{3}{2M\rho R^2} + \frac{K^2 - 2I_z^2}{2M\rho R^2} + iK_1 \frac{(2L_1 - \omega) - \omega(L_2 + 2/\rho + 1/2)}{MR^2} \right], \quad (11)$$

where  $L_1 = (\sqrt{x^2 + y^2}) \partial/\partial z$  and  $L_2 = \hat{q}$ . In (11) we have omitted terms  $\sim (m/M)^2$ , since the result takes a more compact form in this case. The operator (5) is replaced by the electron Hamiltonian

$$h_\rho = -\frac{\rho^2}{2m} \Delta_r + \sqrt{\rho} V, \quad (12)$$

which reproduces the spectrum of the  $H$  or  $D$  atom in the limit  $R \rightarrow \infty$ , exactly reflecting the isotopic effect.<sup>4</sup>

Although the transformed Hamiltonian in (11) appears to be more compact than the original Hamiltonian (1), its effectiveness is open to question. We have accordingly used the theory outlined above to calculate the binding energy of the "molecule"  $eee^+$ . Variational calculations yield binding energies  $E_b = 0.326$  eV, while the one-level approximation based on Eqs. (5)–(7) yields  $E_H = 0.186$  eV (both results are taken from Ref. 3). The one-level approximation with electron Hamiltonian (12) predicts a binding energy  $E_A = 0.305$  eV. We thus see that the dynamics of the problem is described considerably better by our equation.

I wish to thank V. G. Kadyshevskii, A. B. Pestov, E. A. Solov'ev, Plamen Fiziev, and I. S. Shapiro for useful discussions.

<sup>1</sup>L. D. Landau and E. M. Lifshitz, *Kvantovaya mekhanika*, Fizmatgiz, 1963, p. 328 (Quantum Mechanics: Non-Relativistic Theory, Addison-Wesley, Reading, Mass., 1965).

<sup>2</sup>P. R. Bunker and R. E. Moss, *Mol. Phys.* **33**, 417 (1977).

<sup>3</sup>S. I. Vinitskii and L. I. Ponomarev, *Fiz. Elem. Chastits At. Yadra*, **13**, 1336 (1982) [*Sov. J. Part. Nucl.* **13**, 557 (1982)].

<sup>4</sup>A. V. Matveenko, *Phys. Lett.* **129B**, 11 (1983).

Translated by Dave Parsons

Edited by S. J. Amoretti