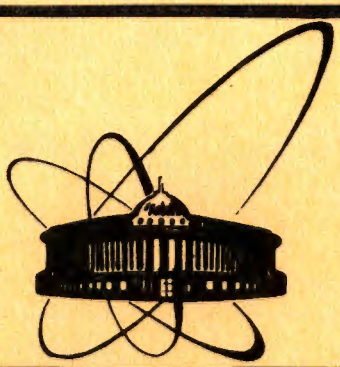

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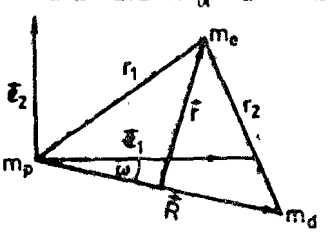
BORN-OPPENHEIMER STATES AND A THREE-BODY PROBLEM

1985

The simplest diatomic molecule consists of two nuclei and a light charged particle and is a particular case of a three-body problem with Coulomb interaction. The Born-Oppenheimer method[1,2] allows a physical separation of variables in this problem by decomposing the total system into a fast and a slow subsystem. Such a decomposition is not unique, and the one minimizing coupling between subsystems in a wider region of the configurational space will be expected the best. After the separation one can follow the classical Born-Oppenheimer procedure: first, the Schrödinger equation is solved for a fast subsystem, then the averaging over its variables is performed, which generates a family of effective potentials and matrix elements defining the motion of a slow subsystem.

In what follows we introduce the transformation of the standard molecular Hamiltonian, which kills the coupling operator between the fast subsystem and the radial motion of the slow subsystem (radial coupling operator). One more transformation changes the coupling operator between the fast subsystem and angular variables of the slow subsystem. These transformations force one to redefine the standard Hamiltonian of the fast subsystem (the classical two-center problem). A new definition of the dynamic two-center problem with an important property is introduced: its spectrum reproduces exactly the spectrum of the product of the molecule dissociation and provides a total separation of variables in the dissociation limit.

As an example we choose molecule HD^+ consisting of proton with mass m_p, deuteron with mass m_d and electron with mass m_e.



In the c.m. system we use the spherical coordinates $\{R, \Theta, \Phi\}$ for the vector $\vec{R}$ and spheroidal coordinates for the vector $\vec{r}\,(x,y,z)$

$$\xi=(r_1+r_2)/R\,,\quad \eta=(r_1-r_2)/R\,,\quad \varphi=\operatorname{arctg}(y/x). \tag{1}$$

The problem Hamiltonian in these variables is

$$H=h-\frac{1}{2M}\left(\frac{1}{R}+\frac{\partial}{\partial R}\right)^2+\frac{1}{MR}\left(\frac{1}{R}+\frac{\partial}{\partial R}\right)\hat{q}+\frac{\vec{J}^2-2\vec{J}\vec{l}}{2MR^2}-\frac{\left(\vec{r}+\frac{\varkappa\vec{R}}{2}\right)^2}{2MR^2}\Delta_{\vec{r}} \tag{2}$$

$$d\vec{R}\,d\vec{r}=R^5 dR\,\frac{\xi^2-\eta^2}{8}\,d\xi\,d\eta\sin\Theta\,d\Theta\,d\Phi\,d\varphi.$$

Here $\vec{J}$ and $\vec{l}$ are the operators of the total angular momentum and electron angular momentum with respect to the c.m.s. of nuclei. The Descartes unit vectors of $\vec{r}$ coincide with the spherical unit vectors of $\vec{R}$ (rotating coordinate system): $\vec{e}_\Theta=\vec{e}_x$, $\vec{e}_\Phi=\vec{e}_y$, $\vec{e}_R=\vec{e}_z$

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

$$\hat{q}=r\frac{\partial}{\partial z}+\frac{\varkappa R}{2}\frac{\partial}{\partial z}\,,\qquad \varkappa=\frac{m_p-m_d}{m_p+m_d}$$

and the reduced masses are given by

$$\frac{1}{m}=\frac{1}{m_e}+\frac{1}{m_p+m_d}\,,\qquad \frac{1}{M}=\frac{1}{m_p}+\frac{1}{m_d}\,. \tag{4}$$

The Hamiltonian of the fast subsystem (two-center problem) is

$$h=-\frac{1}{2m}\Delta_{\vec{r}}+\bar{V}\,,\qquad \bar{V}=-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{R}\,. \tag{5}$$

The classical Born-Oppenheimer theory[1,2] uses the eigenfunctions of the operator (5) as a basis for the expansion of the wave function of the total problem

$$H\Psi(\vec{R},\vec{r})=E\Psi(\vec{R},\vec{r}). \tag{2a}$$

Thus, in the simplest approximation

$$\Psi(\vec{R},\vec{r})=\varphi(R)\,\varphi(\vec{r};R), \tag{6}$$

where $\varphi(\vec{r};R)$ is the wave function of the ground state of the two-center problem

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

Approximation (6) turns out to be rather accurate if electron serves as a light particle but unsatisfactory from the formal point of view, since the solutions of problem (5a) as $Rr_i\to\infty$ become the solutions for the hydrogen atom with the reduced mass m (4) which is neither H nor D atom reduced mass. This formal reasoning is essential since an attempt to make approximation (5a) more accurate in the form

$$\Psi(\vec{R},\vec{r})=\sum_\alpha \varphi_\alpha(\vec{R})\,\varphi_\alpha(\vec{r};R) \tag{6a}$$

leads to the equations for $\varphi_\alpha(\vec{R})$ which happen to be coupled in the asymptotic region ($Rr_i\to\infty$).

We aim at generalizing the Born-Oppenheimer method to the systems of three particles with comparable masses, therefore the definition of the fast subsystem by (5) does not satisfy us by no means.

Now we define the generator

$$\Lambda=\ln(\sqrt{\rho})\,R\left(\frac{1}{R}+\frac{\partial}{\partial R}\right)$$
$$\rho=1+4\alpha\left(\vec{r}+\frac{\varkappa\vec{R}}{2}\right)^2\,,\qquad \alpha=\frac{m}{4M} \tag{7}$$

and using it construct the Hamiltonian

$$H_\Lambda=e^{-\Lambda}He^{\Lambda}=h_\Lambda-\frac{1}{2M}\left(\frac{\partial^2}{\partial R_\Lambda^2}+\frac{5}{R_\Lambda}\frac{\partial}{\partial R_\Lambda}\right)-\frac{3}{2MR_\Lambda^2}+\rho\,\frac{\vec{J}^2-2\vec{J}\vec{l}}{2MR_\Lambda^2}$$
$$d\vec{R}_\Lambda\,d\vec{r}=R_\Lambda^5 dR_\Lambda\,\frac{\xi^2-\eta^2}{8\rho^2}\,d\xi\,d\eta\sin\Theta\,d\Theta\,d\Phi\,d\varphi. \tag{8}$$

In H_Λ there arrises the Hamiltonian of the dynamic two-center problem

$$h_\Lambda=-\frac{1}{2m}\rho^2\Delta_{\vec{r}}+\sqrt{\rho}\,\bar{V} \tag{9}$$
$$d\vec{r}=R_\Lambda^3\,\frac{\xi^2-\eta^2}{8\rho^2}\,d\xi\,d\eta\,d\varphi$$

the spectrum of which turns into that of $H(i=1)$ or $D(i=2)$ atom in the $Rr_i\to\infty$ limit [3,4].

A formal calculation of the operator H_Λ has been made in ref.[3]. The physical meaning of the isometric transformation (8) has been thoroughly studied in ref.[4]. It was shown that the transformation is equivalent to the change of the wave function $\Psi\to\sqrt{\rho}\,\Psi_\Lambda$

and variable $R \to R_\Lambda / \sqrt{\rho}$. The first change is due to nonunitarity of transformation (8) and the second one to redefinition of partial derivatives with respect to variables of a fast subsystem. These properties of a new representation follow just from the form of the generator Λ.

In paper[5] we have used the Hamiltonian H_Λ in the one-state Born-Oppenheimer-type approximation (5a,6). The Hamiltonian (9) was used instead of (5). As an example we calculated the binding energy of the eee^+ "molecule". In the variational calculation $E_\vartheta = 0.336$ eV, and the one-state approximation based on eq. (6) provides the value $E_H = 0.186$ eV (both the results are taken from the review[6]). The one-state approximation with the dynamic two-center Hamiltonian (9) provides the value of the binding energy $E_\Lambda = 0.305$ eV. Thus, the physical properties of the problem are described within our approach much better.

The transformation (8) has been introduced to minimize the operator of radial coupling between the fast and slow subsystems. In the general case when $\vec{J}$ differs from zero the Coriolis interaction operator $\vec{J}\cdot\vec{\ell}$ commuting with the generator (7) is responsible for the coupling of the angular variables of the slow subsystem with the coordinates of the fast subsystem. This operator also survives in the $R r_i^{-1} \to \infty$ limit. As has already been mentioned, this fact is thought to be a drawback of the theory. Now we proceed with the construction of the asymptotically correct theory for $\vec{J} \neq 0$.

To start with, we define anew the unit vectors $\vec{e}_1$, $\vec{e}_2$ and $\vec{e}_3$ for the electron motion

$$\vec{e}_1 = e_\theta \sin\varphi - e_\phi \cos\varphi, \quad \vec{e}_3 = \vec{e}_R$$
$$e_2 = e_\theta \cos\varphi + e_\phi \sin\varphi. \tag{10}$$

It can easily be verified that the unit vectors $\vec{e}_2$ and $\vec{e}_3$ define the plane containing all three particles. Further, since the transformation (10) is a simple rotation, the components of the vector $\vec{J}$ are transformed in the same way (10) and in the new coordinate system

$$\vec{J} = \vec{e}_1 J_1 + \vec{e}_2 J_2 + \vec{e}_3 J_3. \tag{11}$$

As a result, $[J_1, J_2] = -iJ_3$ and so on, i.e., J_i have the standard commutation properties.

With this property in mind we construct the Hamiltonian $H_{\Lambda\Omega}$ in the form

$$H_{\Lambda\Omega} = e^{-\Omega} H_\Lambda e^{\Omega}. \tag{12}$$

where $\Omega = -i\omega J_1$ and ω is the angle between the vector $\vec{R}$ and the principal axis of the inertia tensor of the three-body system (it is shown in the figure). The physical meaning of (8) implies the introduction of a generalized dimension of the system, which depends on its hyperradius[4]. In its turn transformation (12) defines the direction of the relevant vector. The Euler angles $\{\alpha, \beta, \gamma\}$ of this direction are given by

$$\operatorname{ctg}(\alpha - \phi) = \cos\theta \operatorname{ctg}\varphi + \operatorname{ctg}\omega \frac{\sin\theta}{\sin\varphi}$$
$$\cos\beta = \cos\theta\cos\omega - \sin\theta\sin\omega\cos\varphi \tag{13}$$
$$\operatorname{tg}\gamma = -\cos\omega \operatorname{ctg}\varphi - \operatorname{ctg}\theta \frac{\sin\omega}{\sin\varphi}.$$

It can be shown that in the asymptotic region when the molecule decomposes into atom and nucleus ($R r_i^{-1} \to \infty$) formulae (13) determine the direction of the vector connecting the c.m.s. of atom and nucleus. Consequently, transformation (12) should improve the asymptotic properties of the Hamiltonian H_Λ. Indeed, calculating $H_{\Lambda\Omega}$ by (12) we get

$$H_{\Lambda\Omega} = h_{\Lambda\Omega} - \frac{1}{2M}\left(\frac{\partial^2}{\partial R_\Lambda^2} + \frac{5}{R_\Lambda}\frac{\partial}{\partial R_\Lambda}\right) - \frac{3}{2MR_\Lambda^2} + T_R$$
$$- \frac{1}{2MR_\Lambda^2}\frac{1}{1-\Delta}\left\{\Delta \cdot J_1^2 + i J_1\left[4\mathcal{L}_1 + 2\rho\Delta\left(\mathcal{L} + \frac{u}{2}\right)\right]\right\}. \tag{14}$$

In this expression

$$T_R = \frac{1}{2}\left(\frac{J_1^2}{I_1} + \frac{J_2^2}{I_2} + \frac{J_3^2}{I_3}\right) \tag{15}$$

is the Hamiltonian of an asymmetric top with the classical expressions for the principal inertia moments I_i. The operators $\mathcal{L}$ and $\mathcal{L}_1$ accounting for the coupling of rotational and vibrational degrees of freedom in the system are

$$\mathcal{L} = \frac{s}{\xi^2 - \eta^2}\left[(\eta + x\xi)\frac{\partial}{\partial\xi} - (\xi + x\eta)\frac{\partial}{\partial\eta}\right]$$
$$\mathcal{L}_1 = \frac{s}{\xi^2 - \eta^2}\left[\eta(\xi^2 - 1)\frac{\partial}{\partial\xi} - \xi(1 - \eta^2)\frac{\partial}{\partial\eta}\right]. \tag{16}$$

Three new quantities u, S and Δ are given by

$$S=\sqrt{(\xi^2-1)(1-\eta^2)},\quad u=\frac{\xi\eta+x}{S},\quad \Delta=4\alpha\frac{S^2}{\rho^2}. \tag{17}$$

Moreover, we write down expressions for I_i and ω

$$I_1=MR_\Lambda^2,\quad I_2=\frac{1}{2}MR_\Lambda^2(1+\sqrt{1-\Delta}),$$
$$I_3=I_1-I_2,\quad \sin 2\omega=2\alpha\frac{(\xi\eta+x)S}{\rho\sqrt{1-\Delta}}. \tag{18}$$

The Hamiltonian of the dynamic two-center problem $h_{\Lambda S}$ starts to be independent of φ and acquires the form

$$h_{\Lambda S}=-\frac{1}{2m}\rho^2\Delta_{\xi\eta}+\sqrt{\rho}V. \tag{19}$$

Here $\Delta_{\xi\eta}$ is the part of the Laplace operator, which depends only on ξ and η. It should be emphasized that in projecting the Hamiltonian (14) onto the state with a given value of the orbital momentum J and parity it will turn into the system of $(J+1)$ Schrödinger equations of the $\{R,\xi,\eta\}$ variables. In this case it is expedient to introduce the two-center problem $h^{JP}_{\Lambda S}$ with exact quantum numbers J and parity p, which becomes in the general case the system of $(J+1)$ Schrödinger equations in two $\{\xi,\eta\}$ variables[9].

The Hamiltonian (14) is the basic result of this paper. It is simpler than the traditional operator (2), it naturally contains the operator of the classical top with the dynamic components of the inertia tensor from the corresponding mechanical three-body problem. In the dissociation limit the Hamiltonian (14) undergoes an exact separation of variables[7].

Note, that the Hamiltonian $H_{\Lambda S}$ is simply related with the corresponding operator in the K-harmonics method[4] which has recently found application in the molecular systems as well[8]. So, we have established the relation between the Born-Oppenheimer method and the method of hyperspherical harmonics in the three-body problem. However, in this paper we have searched for a physically meaningful basis to expand the total wave function of the system, while in the K-harmonics method one uses the solutions of the free Schrödinger equation for the same purpose.

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Матвеенко А.В. E4-85-372
Метод Борна-Оппенгеймера и задача трех тел

Метод Борна-Оппенгеймера /адиабатический метод/ состоит в физическом разбиении динамической системы на быструю и медленную подсистемы. Он успешно применяется для расчета системы из трех частиц с кулоновским взаимодействием, хотя и является асимптотически некорректным. Предлагается два последовательных преобразования стандартного гамильтониана Борна-Оппенгеймера, которые улучшают его асимптотическое поведение и ведут, одновременно, к переопределению исходных быстрой и медленной подсистем.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Matveenko A.V. E4-85-372
Born-Oppenheimer States and a Three-Body Problem

The author has recently introduced the exact transformation of the standard molecular Hamiltonian, which killed the operator of radial coupling between fast and slow motion thus redefining the Hamiltonian of electronic problem (two-center problem). This leads to a new dynamic two-center problem which reproduces exactly the dissociation limit of a molecule. The coupling operator between agular variables of fast and slow motion (coriolis interaction) can be removed only asymptotically when a molecule dissociates into atom and nucleus. In this limit variables in the total Hamiltonian of the problem are separated completely. This transformation provides the theory with mechanical characteristics of the physical system, inertia tensor components, that gives grounds for the comparison of the present Hamiltonian with that in the K-harmonic method.

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

Communication of the Joint Institute for Nuclear Research. Dubna 1985