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On the exact rotational and internal Hamiltonian for a non-relativistic closed many-body system

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Abstract. Without applying Born-Oppenheimer approximation, the non-relativistic Hamiltonian can be separated into Hamiltonians for the translation of the center of mass and for the rotational and internal motions of the closed many-body system. This exact rotational and internal Hamiltonian can be expressed in terms of three Euler angles for three independent rotations of the system and the rotated Jacobi coordinates for the internal motions.

1. Introduction

In the realm of non-relativistic quantum mechanics of molecules, the original form of the total Hamiltonian can be separated into Hamiltonians for translational and non-translational motions. One usually first applies Born-Oppenheimer approximation (BOA) to separate the non-translational motion into the motions of electrons and nuclei and then separate the nuclear motions into the rotational and vibrational motions [1]. But for a closed many-body system consisting of arbitrary interacting particles (including muons for example), where BOA cannot be applied, the Hamiltonian cannot be separated into Hamiltonians of specific particle sorts. In this case, one can still rewrite the non-translational Hamiltonian specifically for the rotational and internal motions of the system, that can be described separately by three Euler angles and by the rotated Jacobi coordinates. In this work, we derive this form of the rotational and internal Hamiltonian for an arbitrary non-relativistic closed many-body system (for H_2^+ and its isotopomers, see Ref. [2]). To the best of our knowledge, such derivation has not been performed since the first publication of the Schrödinger equation [3]. In addition, we derive the general expression for exact stationary wave functions for the mentioned arbitrary many-body system.

2. Model system

We consider a general non-relativistic closed many-body system without external and spin-dependent interactions. It contains $N \geq 3$ interacting particles with corresponding position vectors $\mathbf{R}_i$ in the laboratory frame (X, Y, Z) and masses m_i. The time-dependent wave function $\Psi(\{\mathbf{R}_i\}, t)$ of this system is the solution of the time-dependent Schrödinger equation $i\hbar\dot{\Psi} = \hat{H}\Psi$, where the time-independent Hamiltonian for two-body interactions (e.g. Coulomb interactions) is equal to the sum of kinetic operators of the particles and two-body potentials $V_{ij} = V_{ji}$ [4]:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{1}{m_i}\nabla_{\mathbf{R}_i}^2 + \sum_{\substack{i,j=1\\ i\neq j}}^{N} V_{ij}(|\mathbf{R}_i - \mathbf{R}_j|). \quad (1)$$

3. Translation of the center of mass

The motion of the system can be separated into the translational motion of the center of mass and the rotational and internal motions of the system. Using Jacobi coordinates (cf. Ref. [4]),

$$\mathbf{r}_j = \mathbf{R}_{j+1} - \frac{1}{M_j}\sum_{i=1}^{j} m_i \mathbf{R}_i \qquad (j = 1, \ldots, N), \tag{2}$$

with $M_j = \sum_{i=1}^{j} m_i$ $(i = 1, \ldots, N)$ and $\mathbf{R}_{N+1} = \mathbf{0}$, the total Hamiltonian (1) is rewritten as

$$\hat{H} = \hat{H}_{\rm trans} + \hat{H}_{\rm rot,int}, \tag{3}$$

where the Hamiltonians for the translational and the rotational and internal motions are

$$\hat{H}_{\rm trans} = -\frac{\hbar^2}{2M}\nabla^2_{\mathbf{r}_{\rm com}}, \tag{4}$$

$$\hat{H}_{\rm rot,int} = -\frac{\hbar^2}{2}\sum_{i=1}^{N-1}\frac{1}{\mu_i}\nabla^2_{\mathbf{r}_i} + 2\sum_{i=1}^{N}\sum_{j=i+1}^{N} V_{ij}\left(\left|\frac{M_{i-1}}{M_i}\,\mathbf{r}_{i-1} - \frac{M_{j-1}}{M_j}\,\mathbf{r}_{j-1} - \sum_{k=i}^{j-1}\frac{m_{k+1}}{M_{k+1}}\,\mathbf{r}_k\right|\right), \tag{5}$$

and the reduced mass μ_i is defined as

$$\mu_i = \left(\frac{1}{M_i} + \frac{1}{m_{i+1}}\right)^{-1} \qquad (i = 1, \ldots, N-1). \tag{6}$$

Furthermore, the total mass of the system and the position vector of the center of mass are defined as $M = M_N$ and $\mathbf{r}_{\rm com} = -\mathbf{r}_N$, respectively. We note that there is no mass-polarization term in the Hamiltonian for the rotational and internal motions, as reported in Refs. [2, 5], because we do not consider the nuclear center of mass but the total center of mass.

4. Rotation of the many-body system

The non-translational motion of the system can in turn be separated into the rotational motion and the internal motion of the many-body system. We use Euler angles (Ψ, Θ, Φ) to describe three independent rotations of the system in the standard-y-convention, i.e., the coordinate system is rotated by the angle Ψ around the initial Z-axis, then by the angle Θ around the new Y-axis, and finally by the angle Φ around the final Z-axis. The corresponding rotation matrices are

$$R_Z(\Psi) = \begin{pmatrix} \cos\Psi & \sin\Psi & 0 \\ -\sin\Psi & \cos\Psi & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{7}$$

$$R_{Y'}(\Theta) = \begin{pmatrix} \cos\Theta & 0 & -\sin\Theta \\ 0 & 1 & 0 \\ \sin\Theta & 0 & \cos\Theta \end{pmatrix}, \tag{8}$$

$$R_{Z''}(\Phi) = \begin{pmatrix} \cos\Phi & \sin\Phi & 0 \\ -\sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{9}$$

The coordinates of N particles in the rotated system $(x, y, z) = (X''', Y''', Z''')$ with reference to the center of mass are calculated as

$$\mathbf{Q}_i = R(\Psi, \Theta, \Phi)\,(\mathbf{R}_i - \mathbf{r}_{\rm com}) \qquad (i = 1, \ldots, N), \tag{10}$$

where the total rotation matrix is

$$R(\Psi,\Theta,\Phi) \;=\; R_{Z''}(\Phi)R_{Y'}(\Theta)R_Z(\Psi). \tag{11}$$

Furthermore, we define the rotated Jacobi coordinates in the rotated system (x,y,z) as

$$\mathbf{q}_j \;=\; \mathbf{Q}_{j+1} - \frac{1}{M_j}\sum_{i=1}^{j} m_i\mathbf{Q}_i \;=\; R(\Psi,\Theta,\Phi)\mathbf{r}_j \qquad (j=1,\ldots,N-1). \tag{12}$$

In order to fix the spatial orientation of the coordinates $\mathbf{q}_j$, we choose Euler angles (Ψ,Θ,Φ) such that $\mathbf{q}_{N-2}=(0,0,R)^T$ with $R\geq 0$, and $\mathbf{q}_{N-1}=(\rho,0,\zeta)^T$ with $\rho\geq 0$. These coordinates for $N=3$ are in accordance with the Jacobi coordinates of the nuclei and the electron of the H_2^+ molecule. The inverse transformation of Eq. (12) is

$$\mathbf{r}_j \;=\; R^T(\Psi,\Theta,\Phi)\mathbf{q}_j \qquad (j=1,\ldots,N-1), \tag{13}$$

where $R^T(\Psi,\Theta,\Phi)$ is the transpose matrix of $R(\Psi,\Theta,\Phi)$. Both sides of Eq. (13) have $3(N-1)$ independent coordinates, containing $3(N-2)$ rotated Jacobi coordinates in $\mathbf{q}_i$ $(i=1,\ldots,N-1)$ and 3 Euler angles (Ψ,Θ,Φ). Then, the Hamiltonian for the rotational and internal motions (5) is rewritten as

$$\begin{aligned}
\hat{H}_{\rm rot,int} \;=\;& -\frac{\hbar^2}{2}\sum_{i=1}^{N-3}\frac{1}{\mu_i}\nabla^2_{\mathbf{q}_i} - \frac{\hbar^2}{2\mu_{N-1}}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{\partial^2}{\partial\zeta^2}\right)\\
&-\frac{\hbar^2}{2\mu_{N-2}}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\frac{1}{2\mu_{N-1}}\frac{1}{\rho^2}\hat{\mathcal{J}}^2_{N-1\,z}\\
&+\frac{1}{4\mu_{N-2}}\frac{1}{R^2}\left(\sum_{i,j=1}^{N-1}\left(\hat{\mathcal{J}}_{i+}\hat{\mathcal{J}}_{j-}+\hat{\mathcal{J}}_{i-}\hat{\mathcal{J}}_{j+}\right)+\hbar\frac{\zeta}{\rho}\sum_{i=1}^{N-1}\left(\hat{\mathcal{J}}_{i+}-\hat{\mathcal{J}}_{i-}\right)\right)\\
&+2\sum_{i=1}^{N}\sum_{j=i+1}^{N}V_{ij}\left(\left|\frac{M_{i-1}}{M_i}\,\mathbf{q}_{i-1}-\frac{M_{j-1}}{M_j}\,\mathbf{q}_{j-1}-\sum_{k=i}^{j-1}\frac{m_{k+1}}{M_{k+1}}\,\mathbf{q}_k\right|\right).
\end{aligned} \tag{14}$$

For the H_2^+ molecule $(N=3)$, this Hamiltonian is similar to that of Ref. [2]. In Eq. (14), the angular momentum operators are defined as

$$\hat{\mathcal{J}}_{i\pm} \;=\; \begin{cases} e^{\pm i\phi_i}\left(\frac{\zeta_i}{\rho_i}\,\hat{\mathcal{J}}_{iz}\pm\hbar\left(\rho_i\frac{\partial}{\partial\zeta_i}-\zeta_i\frac{\partial}{\partial\rho_i}\right)\right) & (i=1,\ldots,N-3)\\ -i\hbar e^{\mp i\Phi}\left(-\frac{1}{\sin\Theta}\frac{\partial}{\partial\Psi}\pm i\,\frac{\partial}{\partial\Theta}+\cot\Theta\frac{\partial}{\partial\Phi}\right) & (i=N-2)\\ \frac{\zeta}{\rho}\,\hat{\mathcal{J}}_{N-1\,z}\pm\hbar\left(\rho\frac{\partial}{\partial\zeta}-\zeta\frac{\partial}{\partial\rho}\right) & (i=N-1)\end{cases}, \tag{15}$$

$$\hat{\mathcal{J}}_{iz} \;=\; \begin{cases} -i\hbar\frac{\partial}{\partial\phi_i} & (i=1,\ldots,N-3)\\ -i\hbar\,\frac{\partial}{\partial\Phi} & (i=N-2)\\ -i\hbar\,\frac{\partial}{\partial\Phi}-\sum_{j=1}^{N-3}\hat{\mathcal{J}}_{jz} & (i=N-1)\end{cases}, \tag{16}$$

and ρ_i, ζ_i, ϕ_i are the cylindrical coordinates of $\mathbf{q}_i$ $(i=1,\ldots,N-3)$. The Hamiltonian $\hat{H}_{\rm rot,int}$ commutes with $\hat{\mathbf{J}}^2$ and $\hat{J}_Z=-i\hbar\frac{\partial}{\partial\Psi}$ but not with $\hat{\mathcal{J}}_{iz}$ $(i=1,\ldots,N-1)$. On the other hand, $\hat{\mathbf{J}}^2$, $\hat{J}_Z$, $\hat{\mathcal{J}}_{iz}$ $(i=1,\ldots,N-1)$ commute among each other. The normalized angular eigenfunctions of these $N+1$ operators are written as

$$\mathcal{D}^{J*}_{M,T,T_1,\ldots,T_{N-3}}(\Psi,\Theta,\Phi,\phi_1,\ldots,\phi_{N-3}) \;=\; \sqrt{\frac{2J+1}{8\pi^2\,(2\pi)^{N-3}}}\,D^{J*}_{M,T}(\Psi,\Theta,\Phi)\prod_{i=1}^{N-3}e^{iT_i\phi_i}, \tag{17}$$

where $D^{J*}_{M,T}(\Psi,\Theta,\Phi)$ is the complex conjugate of the Wigner D-matrix [6]. The quantum numbers for rotation are $J\in\mathbb{N}_0$, $M,T\in\{-J,-J+1,\ldots,J-1,J\}$, $T_i\in\mathbb{Z}$ $(i=1,\ldots,N-3)$.

5. Stationary wave functions of the many-body system

The Hamiltonian $\hat{H}_{\rm rot,int}$ commutes not only with $\hat{\mathbf{J}}^2$ and $\hat{J}_Z$ but also with the parity operator $\hat{\Pi}$ with respect to the center of mass. The solutions of the time-independent Schrödinger equation for the rotational and internal motions,

$$\begin{aligned} & \hat{H}_{\rm rot,int}\Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,\ldots,\mathbf{q}_{N-3}) \\ = \;& E_{J,M,\Pi,n}\Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,\ldots,\mathbf{q}_{N-3}), \end{aligned} \tag{18}$$

are the stationary wave functions $\Psi_{J,M,\Pi,n}$ and the corresponding eigenenergies $E_{J,M,\Pi,n}$ that depend on quantum numbers $J \in \mathbb{N}_0$, $M \in \{-J,-J+1,\ldots,J-1,J\}$ for the rotational motion, $n \in \mathbb{N}_0$ for the internal motion, and $\Pi \in \{-1,+1\}$ for the parity of the many-body system. Since the Hamiltonian $H_{\rm rot,int}$ does not commute with $\hat{\mathcal{J}}_{iz}$ $(i = 1,\ldots,N-1)$, the stationary wave functions $\Psi_{J,M,\Pi,n}$ can be expanded as

$$\begin{aligned} & \Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,\ldots,\mathbf{q}_{N-3}) \\ = \;& \sum_{T=-J}^{J}\sum_{\{T_i\}}\mathcal{D}^{J*}_{M,T,\{T_i\}}(\Psi,\Theta,\Phi,\{\phi_i\})\psi_{J,M,T,\{T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\}), \end{aligned} \tag{19}$$

where $\psi_{J,M,T,\{T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\})$ are the real and even wavefunctions. Using the parity relation for the Wigner D-matrix,

$$\hat{\Pi}D^{J*}_{M,T}(\Psi,\Theta,\Phi) \;=\; (-1)^{J+T}D^{J*}_{M,-T}(\Psi,\Theta,\Phi), \tag{20}$$

we are able to show that the following relation must be satisfied:

$$\psi_{J,M,-T,\{-T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\}) \;=\; (-1)^{J+T}\Pi\psi_{J,M,T,\{T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\}). \tag{21}$$

Finally, with

$$\tilde{\psi}_{J,M,T,\{T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\}) \;=\; \begin{cases} \frac{1}{2}\psi_{J,M,0,\{T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\}) & T=0 \\ \psi_{J,M,T,\{T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\}) & T\neq 0 \end{cases}, \tag{22}$$

we obtain the general expression for the stationary wave functions as

$$\begin{aligned} & \Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\{\mathbf{q}_i\}) \\ = \;& \sum_{T=0}^{J}\sum_{\{T_i\}}\Big(\mathcal{D}^{J*}_{M,T,\{T_i\}}(\Psi,\Theta,\Phi,\{\phi_i\}) + (-1)^{J+T}\Pi\mathcal{D}^{J*}_{M,-T,\{-T_i\}}(\Psi,\Theta,\Phi,\{\phi_i\})\Big) \\ & \qquad \tilde{\psi}_{J,M,T,\{T_i\},n}(R,\rho,\zeta,\{\rho_i\},\{\zeta_i\}). \end{aligned} \tag{23}$$

6. Conclusion

We have derived the exact rotational and internal Hamiltonian for an arbitrary non-relativistic closed many-body system and the corresponding stationary wave functions, where the rotational and internal motions of the system can be described separately by three Euler angles and by the rotated Jacobi coordinates.

References

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