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Probability and Flux Densities in the Center-of-Mass Frame

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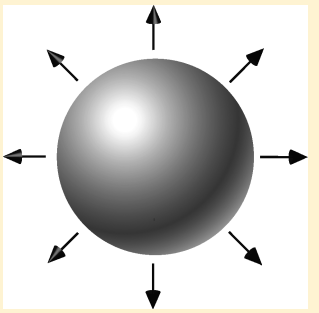
ABSTRACT: For an arbitrary nonstationary wave function of a nonrelativistic closed many-body system consisting of arbitrary interacting particles, the general expressions for the time-dependent one-particle probability and flux densities in the center-of-mass frame without applying Born−Oppenheimer approximation are obtained. Even the wave function for the translation is additionally introduced; it disappears in the center-of-mass frame automatically. It is shown that for the rotational ground state the time-dependent probability and flux densities of an arbitrary particle in the center-of-mass frame are isotropic. It means that the angular dependence is absent but these densities depend on radius and time. More importantly, it is shown that the angular components of the time-dependent flux density vanish. With these statements, one can calculate the radial component of the radius- and time-dependent electronic flux density within the Born−Oppenheimer approximation via the continuity equation. Application of this theory to the pulsating or exploding "quantum bubble" of the vibrating or dissociating Na_2 molecule in the rotational ground state, respectively, is found elsewhere in this issue.



1. INTRODUCTION

The well-known Born−Oppenheimer approximation[1] (BOA) is widely used in the realm of quantum chemistry and quantum dynamics of molecules. Because the electron is much lighter than the nucleus, one can obtain the approximate total wave function of the molecule by separating the molecular motion into the motions of electrons and nuclei. In a single (nondegenerate) electronic state, the total wave function is then approximately equal to the product of the real electronic wave function and the (in general time-dependent) pure nuclear wave function that often describes the molecular vibrations and rotations. Within the BOA, one can calculate electronic and nuclear probability densities as well as the nuclear flux density that all depend in general on time, but due to the real electronic wave function, it is impossible to get nonzero electronic flux density directly from the well-known formula for the flux density that is derived from the time-dependent Schrödinger equation. This nonapplicability is of course trivial, because the electronic wave function in the BOA limit does not obey the time-dependent Schrödinger equation. A possible way out within the BOA is the calculation of the electronic flux instead of the electronic flux density via the continuity equation.[2]

An elegant idea to overcome this BOA dilemma for the time-dependent electronic flux density is that the vibrating or dissociating molecule is in the rotational ground state where the rotational quantum numbers are zero ($J = M = 0$); i.e., the molecule is no longer prealigned and its alignment is equally distributed in space. For vibrating or dissociating diatomic molecules such as H_2^+ and Na_2 in a single electronic and rotational ground state,[3−6] it has been already shown that the time-dependent electronic and nuclear probability densities within the BOA are isotropic. It is the generalization of the statement for time-independent systems in a single and thus real-valued ground state with zero orbital angular momentum that the time-independent probability density is isotropic,[7−9] and hence the corresponding flux density is exactly zero. For vibrating or dissociating diatomic molecules possessing a time-dependent one-dimensional vibrational wave function, it has been showed that the time-dependent nuclear flux density is isotropic and its angular components vanish.[3,4,6] However, it has been *assumed* that the angular components of the time-dependent electronic flux density vanish, too. Then, the radial component of the time-dependent electronic flux denisty can be calculated via the continuity equation and is also isotropic. Hence, the vibrating or dissociating system in a single electronic and rotational ground state appears as a pulsating or exploding "quantum bubble", respectively.[3,4,6] To validate these results, one still has to prove analytically that the angular components of the time-dependent electronic flux density vanish and it will be done in this work.

Of course, it would not at all be trivial to prove within the BOA that only the angular but not the radial components of the electronic flux density vanish because the electronic wave function of a single electronic state is real and the electronic flux density within the BOA is always zero. Therefore, one has to go beyond the BOA. Once it is proven, then one can expect that it is also applicable within the BOA. If the electronic probability density within the BOA is a good approximation to the exact electronic probability density, then one can use the continuity equation to find a good approximation to the exact electronic flux density. Furthermore, it is not restricted to a

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single electronic state or to the molecular system. To generalize the analysis, an arbitrary nonstationary wave function of a nonrelativistic closed many-body system consisting of arbitrary interacting particles is considered where the general expressions for the exact stationary wave functions of this system have been already derived.[10] In this work, the general expressions for the time-dependent one-particle probability and flux densities in the center-of-mass frame are derived and it is proven that for the rotational ground state the angular components of the flux density always vanish and the corresponding radial component as well as the probability density are isotropic.

Although the translation of the closed many-body system is introduced in the laboratory frame, its wave function completely disappears in the center-of-mass frame, in which the point of origin is the center of mass of all particles and not the specific center of mass, e.g., nuclear center of mass that leads to the additional mass-polarization term in the Hamiltonian.[10−12] In general, the probability and flux densities in the laboratory frame with nonspherical wave function for the translation cannot be isotropic. Translational effects on prealigned electronic and nuclear ring currents in hydrogen-like systems (i.e., not in the rotational ground state of the system) have been already investigated,[13] where ring currents can be induced by a circularly polarized laser pulse.[14] A simplified analysis for the system with spherical wave function for the translation could be carried out and it would lead to the isotropic distribution of the probability and flux densities in the laboratory frame, if the corresponding densities in the center-of-mass frame are isotropic. Because it does not change the conclusion, the center-of-mass frame (equivalent to the laboratory frame without translation) is therefore used in this work to investigate the symmetry properties of the probability and flux densities.

The model of the many-body system along with the corresponding nonstationary wave function including the wave function for the translation is defined in section 2. In section 3, the time-dependent one-particle probability density in the center-of-mass frame is derived. A very similar derivation in section 4 is done for the time-dependent one-particle flux density in the center-of-mass frame. In both these sections, the symmetry properties of the probability and flux densities in the rotational ground state are revealed. Section 5 concludes this work.

2. MODEL SYSTEM

Here, a nonrelativistic closed many-body system consisting of $N \geq 3$ interacting particles without external and spin-dependent interactions is considered.[10] Although these N particles can have spins, the theory described here does not use symmetric or antisymmetric wave functions for bosons and fermions, respectively. However, it can be generalized to the theory for particles with spin, to be published elsewhere, but it has no influence on the symmetry properties of probability and flux densities after integration over all spin variables. Therefore, in this work only distinguishable particles are considered.

In the center-of-mass frame, the stationary wave function of the exact rotational and internal Hamiltonian for this system is denoted as $\Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3})$, where $J \in \mathbb{N}_0$ and $M \in \{-J, -J+1, ..., J-1, J\}$ are the rotational quantum numbers, $\Pi \in \{-1, +1\}$ is the quantum number for the parity of the many-body system, and $n \in \mathbb{N}_0$ is the quantum number for the internal motion.[10] Furthermore, Ψ, Θ, Φ are Euler angles for three independent rotations of the system and $\mathbf{q}_1, ..., \mathbf{q}_{N-3}, \mathbf{q}_{N-2} = (0, 0, R)^T, \mathbf{q}_{N-1} = (\rho, 0, \zeta)^T$ $(R \geq 0, \rho \geq 0)$ are the rotated Jacobi coordinates for $3N-6$ independent internal motions.[10] The corresponding stationary eigenenergy is denoted as $E_{J,M,\Pi,n}$ and the stationary wave function is normalized, i.e.

$$\int d\mathbf{r}_1 ... \int d\mathbf{r}_{N-1} \, |\Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3})|^2 = 1 \tag{1}$$

The nonrotated Jacobi coordinates $\mathbf{r}_1, ..., \mathbf{r}_{N-1}$ (after separation of translation of the center of mass) are connected to the rotated Jacobi coordinates $\mathbf{q}_1, ..., \mathbf{q}_{N-1}$ according to[10]

$$\mathbf{q}_i = \hat{R}(\Psi,\Theta,\Phi)\mathbf{r}_i \qquad (i = 1, ..., N-1) \tag{2}$$

where $\hat{R}(\Psi,\Theta,\Phi)$ is the rotation matrix

$$\hat{R}(\Psi,\Theta,\Phi) = \begin{pmatrix} \cos\Phi & \sin\Phi & 0 \\ -\sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\Theta & 0 & -\sin\Theta \\ 0 & 1 & 0 \\ \sin\Theta & 0 & \cos\Theta \end{pmatrix} \begin{pmatrix} \cos\Psi & \sin\Psi & 0 \\ -\sin\Psi & \cos\Psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{3}$$

In the laboratory frame, there is an additional wave function describing the translation of the center of mass. It is denoted as $\Psi_{tr}(\mathbf{r}_{com},t)$, where $\mathbf{r}_{com}$ is the position vector of the center of mass. This wave function is normalized, i.e.

$$\int d\mathbf{r}_{com} \, |\Psi_{tr}(\mathbf{r}_{com},t)|^2 = 1 \tag{4}$$

In general, the time-dependent (nonstationary) total wave function is written as the product of the wave function for the translation and the superposition of stationary wave functions with corresponding time-dependent exponential factors, i.e.

$$\Psi_{tot}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3},\mathbf{r}_{com},t) = \Psi_{tr}(\mathbf{r}_{com},t) \times \sum_{J,M,\Pi,n} C_{J,M,\Pi,n} \Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3}) e^{-iE_{J,M,\Pi,n}t/\hbar} \tag{5}$$

with the normalization condition for time-independent coefficients

$$\sum_{J,M,\Pi,n} |C_{J,M,\Pi,n}|^2 = 1 \tag{6}$$

3. PROBABILITY DENSITY

The time-dependent probability density of the ith particle as a function of the position vector $\mathbf{R} = \mathbf{R}_i - \mathbf{r}_{com}$ in the center-of-mass frame is given by

$$\rho_i(\mathbf{R},t) = \int d\mathbf{R}_1 ... \int d\mathbf{R}_N \, \delta(\mathbf{R} - (\mathbf{R}_i - \mathbf{r}_{com})) \times |\Psi_{tot}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3},\mathbf{r}_{com},t)|^2 \tag{7}$$

where $\mathbf{R}_j$ $(j = 1, ..., N)$ is the position vector of the jth particle in the laboratory frame. These position vectors $\mathbf{R}_1, ..., \mathbf{R}_N$ are connected to the nonrotated Jacobi coordinates $\mathbf{r}_1, ..., \mathbf{r}_{N-1}, \mathbf{r}_N = -\mathbf{r}_{com}$ according to[10,15]

$$\mathbf{r}_k = \mathbf{R}_{k+1} - \frac{1}{M_k} \sum_{j=1}^{k} m_j \mathbf{R}_j \qquad (k = 1, ..., N) \tag{8}$$

with $M_k = \sum_{j=1}^{k} m_j$ $(k = 1, ..., N)$, m_j being the mass of the jth particle, and $\mathbf{R}_{N+1} = \mathbf{0}$.

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For the probability density of the ith particle with $i < N$, formula 7 can be rewritten by exchanging the numbering of the ith particle and the Nth particle. Due to this exchange, i.e., $\tilde{\mathbf{R}}_i = \mathbf{R}_N$, $\tilde{\mathbf{R}}_N = \mathbf{R}_i$, and $\tilde{\mathbf{R}}_j = \mathbf{R}_j$ ($j \neq i, N$), new Euler angles $\tilde{\Psi}$, $\tilde{\Theta}$, $\tilde{\Phi}$ and new rotated Jacobi coordinates $\tilde{\mathbf{q}}_1$, ..., $\tilde{\mathbf{q}}_{N-3}$, $\tilde{\mathbf{q}}_{N-2} = (0, 0, \tilde{R})^T$, $\tilde{\mathbf{q}}_{N-1} = (\tilde{\rho}, 0, \tilde{\zeta})^T$ ($\tilde{R} \geq 0, \tilde{\rho} \geq 0$) are obtained but $\tilde{\mathbf{r}}_{com} = \mathbf{r}_{com}$ remains unchanged. Then, formula 7 after renaming all variables by removing the corresponding tildes becomes

$$\rho_i(\mathbf{R},t) = \int d\mathbf{R}_1 ... \int d\mathbf{R}_N \, \delta(\mathbf{R}-(\mathbf{R}_N-\mathbf{r}_{com})) \times |\tilde{\Psi}_{tot}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3},\mathbf{r}_{com},t)|^2 \quad (9)$$

where the new total wave function $\tilde{\Psi}_{tot}$ is in an entirely different form than the original wave function Ψ_{tot} but the translational wave function $\Psi_{tr}(\mathbf{r}_{com},t)$ and the time-independent coefficients $C_{J,M,\Pi,n}$ as well as the eigenenergies $E_{J,M,\Pi,n}$ remain unchanged. Despite the new form of the stationary wave functions for the rotational and internal motions $\tilde{\Psi}_{J,M,\Pi,n}$, the identical expressions (7) and (9) represent the time-dependent probability density of the ith particle and the exchanged Nth particle in the center-of-mass frame, respectively.

Because the stationary wave functions in eq 5 and thus the total wave function are not specified, it is sufficient for investigation of the symmetry properties to evaluate the time-dependent probability density of the Nth particle in the center-of-mass frame as

$$\rho_N(\mathbf{R},t) = \int d\mathbf{R}_1 ... \int d\mathbf{R}_N \delta\,(\mathbf{R}-(\mathbf{R}_N-\mathbf{r}_{com})) \times |\Psi_{tot}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3},\mathbf{r}_{com},t)|^2 \quad (10)$$

Using eq 8, it can be shown that the total volume element $d\mathbf{R}_1...d\mathbf{R}_N$ is transformed as

$$d\mathbf{R}_1...d\mathbf{R}_N = d\mathbf{r}_1...d\mathbf{r}_N \quad (11)$$

and the position vector of the center of mass $\mathbf{r}_{com}$ is expressed as

$$\mathbf{r}_{com} = \mathbf{R}_N - \frac{M_{N-1}}{M_N}\mathbf{r}_{N-1} \quad (12)$$

with the associated volume element $d\mathbf{r}_{com} = d\mathbf{r}_N$. Using the expression for the total wave function (5), the normalization condition (4), and

$$\delta(\mathbf{R}-(\mathbf{R}_N-\mathbf{r}_{com})) = \frac{M_N}{M_{N-1}}\delta\left(\frac{M_N}{M_{N-1}}\mathbf{R} - \mathbf{r}_{N-1}\right) \quad (13)$$

the probability density (10) is rewritten as

$$\rho_N(\mathbf{R},t) = \frac{M_N}{M_{N-1}} \int d\mathbf{r}_1 ... \int d\mathbf{r}_{N-1}\delta\left(\frac{M_N}{M_{N-1}}\mathbf{R}-\mathbf{r}_{N-1}\right) \times \left| \sum_{J,M,\Pi,n} C_{J,M,\Pi,n}\Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,...,\mathbf{q}_{N-3})e^{-iE_{J,M,\Pi,n}t/\hbar}\right|^2 \quad (14)$$

As already mentioned in section 1, the probability density in the center-of-mass frame (14) does not depend on the form of the translational wave function anymore. Integrating over $\mathbf{r}_{N-1}$ yields the replacement of $\mathbf{r}_{N-1}$ according to

$$\mathbf{r}_{N-1} = \frac{M_N}{M_{N-1}}\mathbf{R} \quad (15)$$

Because $\mathbf{r}_{N-1}$ is connected to $\mathbf{q}_{N-1}$ according to eq 2, relation 15 is then rearranged as

$$\mathbf{q}_{N-1} = \frac{M_N}{M_{N-1}}\hat{R}(\Psi,\Theta,\Phi)\mathbf{R} \quad (16)$$

Using the definition for $\mathbf{q}_{N-1}$ introduced in section 2, i.e., $\mathbf{q}_{N-1} = (\rho, 0, \zeta)^T$ with $\rho \geq 0$, and expressing the position vector in spherical coordinates $\mathbf{R} = (\mathcal{R}\cos\phi\sin\theta, \mathcal{R}\sin\phi\sin\theta, \mathcal{R}\cos\theta)^T$, where $\mathcal{R}$ is the radius and ϕ, θ are the angles of the position vector $\mathbf{R}$ in the center-of-mass frame, one obtains from eqs 15 and 16 the expressions for the coordinates ρ, ζ, Φ that depend on $\mathcal{R}$, Ψ, Θ, ϕ, θ as (see ref 16 for the mathematical function $\text{atan2}(y,x) \in [-\pi, \pi]$)

$$\rho(\mathcal{R},\Psi,\Theta,\phi,\theta) = \frac{M_N}{M_{N-1}}\mathcal{R}\sqrt{1 - (\cos(\Psi-\phi)\sin\Theta\sin\theta + \cos\Theta\cos\theta)^2} \quad (17)$$

$$\zeta(\mathcal{R},\Psi,\Theta,\phi,\theta) = \frac{M_N}{M_{N-1}}\mathcal{R}(\cos(\Psi-\phi)\sin\Theta\sin\theta + \cos\Theta\cos\theta) \quad (18)$$

$$\Phi(\Psi,\Theta,\phi,\theta) = \text{atan2}(-\sin(\Psi-\phi)\sin\theta, \cos(\Psi-\phi)\cos\Theta\sin\theta - \sin\Theta\cos\theta) \quad (19)$$

Moreover, using the inverse transformation of (2) for $\mathbf{q}_{N-2} = (0, 0, R)^T$ with $R \geq 0$, one gets

$$\mathbf{r}_{N-2} = \hat{R}^T(\Psi,\Theta,\Phi)\mathbf{q}_{N-2} = (R\cos\Psi\sin\Theta, R\sin\Psi\sin\Theta, R\cos\Theta)^T \quad (20)$$

and it can be shown that the volume elements in eq 14 are transformed according to

$$d\mathbf{r}_{N-2} = R^2\sin\Theta\, dR\, d\Psi\, d\Theta \quad (21)$$

$$d\mathbf{r}_1...d\mathbf{r}_{N-3} = d\mathbf{q}_1...d\mathbf{q}_{N-3} \quad (22)$$

With the transformations (17)−(19), (21), and (22), the expression for the time-dependent probability density (14) in the center-of-mass frame is then rewritten as

$$\rho_N(\mathcal{R},\phi,\theta,t) = \frac{M_N}{M_{N-1}}\int_0^{2\pi} d\Psi \int_0^{\pi} \sin\Theta\, d\Theta \int_0^{\infty} R^2\, dR \int d\mathbf{q}_1 ... \int d\mathbf{q}_{N-3} \left| \sum_{J,M,\Pi,n} C_{J,M,\Pi,n}\Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi(\Psi,\Theta,\phi,\theta),R,\rho(\mathcal{R},\Psi,\Theta,\phi,\theta),\zeta(\mathcal{R},\Psi,\Theta,\phi,\theta),\mathbf{q}_1,...,\mathbf{q}_{N-3})e^{-iE_{J,M,\Pi,n}t/\hbar}\right|^2 \quad (23)$$

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To simplify this integral further, one can choose suitable spherical coordinates Ψ' and Θ' rather than Ψ and Θ with the same volume element

$$\sin\Theta'\,\mathrm{d}\Psi'\,\mathrm{d}\Theta' = \sin\Theta\,\mathrm{d}\Psi\,\mathrm{d}\Theta \tag{24}$$

The spherical coordinates Ψ and Θ are the angles of the vector $\mathbf{r}_{N-2}$ with respect to the z-axis of the center-of-mass frame; see eq 20. Now, the spherical coordinates Ψ' and Θ' are defined as the angles of the vector $\mathbf{r}_{N-2}$ with respect to the position vector $\mathbf{R} \propto \mathbf{r}_{N-1}$ (15). In particular, Θ' is the angle between two vectors $\mathbf{r}_{N-1}$ and $\mathbf{r}_{N-2}$ defined as

$$\Theta'(\Psi,\Theta,\phi,\theta) = \arccos\left(\frac{\zeta(\mathcal{R},\Psi,\Theta,\phi,\theta)}{\sqrt{[\rho(\mathcal{R},\Psi,\Theta,\phi,\theta)]^2 + [\zeta(\mathcal{R},\Psi,\Theta,\phi,\theta)]^2}}\right) \tag{25}$$

It is easily shown using eqs 17 and 18 that the angle Θ' is independent of $\mathcal{R}$ and that

$$\rho(\mathcal{R},\Psi,\Theta,\phi,\theta) = \frac{M_N}{M_{N-1}}\mathcal{R}\sin\Theta'(\Psi,\Theta,\phi,\theta) \tag{26}$$

$$\zeta(\mathcal{R},\Psi,\Theta,\phi,\theta) = \frac{M_N}{M_{N-1}}\mathcal{R}\cos\Theta'(\Psi,\Theta,\phi,\theta) \tag{27}$$

Furthermore, Ψ' is the azimuthal angle of the vector $\mathbf{r}_{N-2}$ with respect to the vector $\mathbf{r}_{N-1}$ defined as

$$\Psi'(\Psi,\Theta,\phi,\theta) = \Phi(\Psi,\Theta,\phi,\theta) \tag{28}$$

Using the inverse functions of eqs 25 and 28, i.e., $\Psi(\Psi',\Theta',\phi,\theta)$ and $\Theta(\Psi',\Theta',\phi,\theta)$, where it is not necessary to express these inverse functions explicitly here, one obtains from eq 23 the general expression for the one-particle probability density in the center-of-mass frame as

$$\rho_N(\mathcal{R},\phi,\theta,t) = \frac{M_N}{M_{N-1}}\int_0^{2\pi}\mathrm{d}\Psi'\int_0^{\pi}\sin\Theta'\,\mathrm{d}\Theta'\int_0^{\infty}R^2\,\mathrm{d}R\int\mathrm{d}\mathbf{q}_1\ldots\int\mathrm{d}\mathbf{q}_{N-3}$$
$$\left|\sum_{J,M,\Pi,n} C_{J,M,\Pi,n}\Psi_{J,M,\Pi,n}(\Psi(\Psi',\Theta',\phi,\theta),\Theta(\Psi',\Theta',\phi,\theta),\Psi',R,\frac{M_N}{M_{N-1}}\mathcal{R}\sin\Theta',\frac{M_N}{M_{N-1}}\mathcal{R}\cos\Theta',\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{J,M,\Pi,n}t/\hbar}\right|^2 \tag{29}$$

It is noticed that the angles ϕ and θ of the position vector $\mathbf{R}$ in the center-of-mass frame only appear as the arguments of the functions Ψ and Θ in eq 29. For the rotational ground state ($J = M = 0$) where the alignment of the many-body system is equally distributed in space, the Wigner function[17] and thus the stationary wave functions[10] do not depend on three angles Ψ, Θ, Ψ'. In this case, the probability density (29) is simplified to

$$\rho_N^{J=M=0}(\mathcal{R},t) = \frac{M_N}{M_{N-1}}2\pi\int_0^{\pi}\sin\Theta'\,\mathrm{d}\Theta'\int_0^{\infty}R^2\,\mathrm{d}R\int\mathrm{d}\mathbf{q}_1\ldots\int\mathrm{d}\mathbf{q}_{N-3}$$
$$\left|\sum_{\Pi,n} C_{0,0,\Pi,n}\Psi_{0,0,\Pi,n}(0,0,0,R,\frac{M_N}{M_{N-1}}\mathcal{R}\sin\Theta',\frac{M_N}{M_{N-1}}\mathcal{R}\cos\Theta',\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{0,0,\Pi,n}t/\hbar}\right|^2 \tag{30}$$

and does not depend on ϕ and θ, but only on $\mathcal{R}$ and t. It means that for the rotational ground state the time-dependent one-particle probability density in the center-of-mass frame is isotropic and depends on radius and time.

4. FLUX DENSITY

As already explained in section 3, it is also sufficient for investigation of the symmetry properties to evaluate the time-dependent flux density of the Nth particle (rather than ith particle in general) in the center-of-mass frame as

$$\mathbf{j}_N(\mathbf{R},t) = \frac{\hbar}{m_N}\int\mathrm{d}\mathbf{R}_1\ldots\int\mathrm{d}\mathbf{R}_N\,\delta(\mathbf{R}-(\mathbf{R}_N-\mathbf{r}_{\mathrm{com}}))$$
$$\mathrm{Im}[(\Psi_{\mathrm{tot}}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,\ldots,\mathbf{q}_{N-3},\mathbf{r}_{\mathrm{com}},t))^*$$
$$\nabla_{\mathbf{R}}\Psi_{\mathrm{tot}}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,\ldots,\mathbf{q}_{N-3},\mathbf{r}_{\mathrm{com}},t)] \tag{31}$$

where the Nabla operator in spherical coordinates is defined as

$$\nabla_{\mathbf{R}} = \mathbf{e}_{\mathcal{R}}\frac{\partial}{\partial\mathcal{R}} + \mathbf{e}_{\theta}\frac{1}{\mathcal{R}}\frac{\partial}{\partial\theta} + \mathbf{e}_{\phi}\frac{1}{\mathcal{R}\sin\theta}\frac{\partial}{\partial\phi} \tag{32}$$

and $\mathbf{e}_{\mathcal{R}}$, $\mathbf{e}_{\theta}$, $\mathbf{e}_{\phi}$ are the unit vectors. Using eqs 4, 5, 11, 12, and 13, $\mathrm{d}\mathbf{r}_{\mathrm{com}} = \mathrm{d}\mathbf{r}_N$, the flux density (31) is rewritten as

$$\mathbf{j}_N(\mathbf{R},t) = \frac{\hbar}{m_N}\frac{M_N}{M_{N-1}}\int\mathrm{d}\mathbf{r}_1\ldots\int\mathrm{d}\mathbf{r}_{N-1}\,\delta\left(\frac{M_N}{M_{N-1}}\mathbf{R}-\mathbf{r}_{N-1}\right)\mathrm{Im}\left[\left(\sum_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}} C_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}}\Psi_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}}t/\hbar}\right)^*\right.$$
$$\left.\nabla_{\mathbf{R}}\sum_{J,M,\Pi,n} C_{J,M,\Pi,n}\Psi_{J,M,\Pi,n}(\Psi,\Theta,\Phi,R,\rho,\zeta,\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{J,M,\Pi,n}t/\hbar}\right] \tag{33}$$

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that is analogous to eq 14 for the probability density. So, the flux density in the center-of-mass frame (33) does not depend on the form of the translational wave function anymore, too. Because the evaluation of the integral in eq 33 is very similar to the evaluation of the integral for the probability density in section 3, it is not necessary to repeat the derivation here. One obtains from (33) the general expression for the one-particle flux density in the center-of-mass frame

$$\mathbf{j}_N(\mathcal{R},\phi,\theta,t) = \frac{\hbar}{m_N}\frac{M_N}{M_{N-1}}\int_0^{2\pi} \mathrm{d}\Psi' \int_0^{\pi} \sin\Theta'\,\mathrm{d}\Theta' \int_0^{\infty} R^2\,\mathrm{d}R \int \mathrm{d}\mathbf{q}_1 \ldots \int \mathrm{d}\mathbf{q}_{N-3}$$
$$\mathrm{Im}\left[\left(\sum_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}} C_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}}\Psi_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}}(\Psi(\Psi',\Theta',\phi,\theta),\Theta(\Psi',\Theta',\phi,\theta),\Psi',R,\frac{M_N}{M_{N-1}}\mathcal{R}\sin\Theta',\frac{M_N}{M_{N-1}}\mathcal{R}\cos\Theta',\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{\tilde{J},\tilde{M},\tilde{\Pi},\tilde{n}}t/\hbar}\right)^*\right.$$
$$\left.\nabla_{\mathbf{R}}\sum_{J,M,\Pi,n} C_{J,M,\Pi,n}\Psi_{J,M,\Pi,n}(\Psi(\Psi',\Theta',\phi,\theta),\Theta(\Psi',\Theta',\phi,\theta),\Psi',R,\frac{M_N}{M_{N-1}}\mathcal{R}\sin\Theta',\frac{M_N}{M_{N-1}}\mathcal{R}\cos\Theta',\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{J,M,\Pi,n}t/\hbar}\right] \quad (34)$$

that is analogous to eq 29 for the probability density. A similar conclusion is obtained for the flux density: For the rotational ground state ($J = M = 0$), the wave function does not depend on Ψ, Θ, Ψ' and in this case the flux density (34) using eq 32 is simplified to

$$\mathbf{j}_N^{J=M=0}(\mathcal{R},t) = \frac{\hbar}{m_N}\frac{M_N}{M_{N-1}}2\pi\int_0^{\pi} \sin\Theta'\,\mathrm{d}\Theta' \int_0^{\infty} R^2\,\mathrm{d}R \int \mathrm{d}\mathbf{q}_1 \ldots \int \mathrm{d}\mathbf{q}_{N-3}$$
$$\mathrm{Im}\left[\left(\sum_{\tilde{\Pi},\tilde{n}} C_{0,0,\tilde{\Pi},\tilde{n}}\Psi_{0,0,\tilde{\Pi},\tilde{n}}(0,0,0,R,\frac{M_N}{M_{N-1}}\mathcal{R}\sin\Theta',\frac{M_N}{M_{N-1}}\mathcal{R}\cos\Theta',\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{0,0,\tilde{\Pi},\tilde{n}}t/\hbar}\right)^*\right.$$
$$\left.\frac{\partial}{\partial\mathcal{R}}\sum_{\Pi,n} C_{0,0,\Pi,n}\Psi_{0,0,\Pi,n}(0,0,0,R,\frac{M_N}{M_{N-1}}\mathcal{R}\sin\Theta',\frac{M_N}{M_{N-1}}\mathcal{R}\cos\Theta',\mathbf{q}_1,\ldots,\mathbf{q}_{N-3})\mathrm{e}^{-\mathrm{i}E_{0,0,\Pi,n}t/\hbar}\right]\mathbf{e}_{\mathcal{R}} \quad (35)$$

and does not depend on ϕ and θ, but only on $\mathcal{R}$ and t, too. Thus, for the rotational ground state the time-dependent one-particle flux density in the center-of-mass frame is also isotropic and depends on radius and time. In addition, as shown in eq 35, the angular components of the flux density exactly vanish for the rotational ground state.

In general, the probability density (29) and flux density (34) of the ith particle obey the continuity equation

$$\frac{\partial}{\partial t}\rho_i(\mathbf{R},t) + \nabla\cdot\mathbf{j}_i(\mathbf{R},t) = 0 \quad (36)$$

Due to the disappearance of the angular components of the flux density in the rotational ground state ($J = M = 0$), this equation is simplified to

$$\frac{\partial}{\partial t}\rho_i^{J=M=0}(\mathcal{R},t) + \frac{1}{\mathcal{R}^2}\frac{\partial}{\partial\mathcal{R}}\mathcal{R}^2 j_{\mathcal{R},i}^{J=M=0}(\mathcal{R},t) = 0 \quad (37)$$

where the divergence in spherical coordinates is used and $j_{\mathcal{R},i}^{J=M=0}(\mathcal{R},t) = \mathbf{j}_i^{J=M=0}(\mathcal{R},t)\cdot\mathbf{e}_{\mathcal{R}}$ is the radial component of the flux density of the ith particle. The continuity equation for the rotational ground state (37) is universally valid. So, within the BOA, one can assume that this continuity equation is also valid, although the radial component of the electronic flux density cannot be obtained directly from the well-known formula for the flux density if only a single electronic state is used.[3] One can rewrite eq 37 into

$$j_{\mathcal{R},i}^{J=M=0}(\mathcal{R},t) = -\frac{1}{\mathcal{R}^2}\int_0^{\mathcal{R}} \mathcal{R}'^2\frac{\partial}{\partial t}\rho_i^{J=M=0}(\mathcal{R}',t) \quad (38)$$

where the boundary condition

$$\lim_{\mathcal{R}\to 0}\mathcal{R}^2 j_{\mathcal{R},i}^{J=M=0}(\mathcal{R},t) = 0 \quad (39)$$

is assumed.[3,6] Hence, the flux density in the rotational ground state can be obtained via the continuity equation 38. Within the BOA, the electronic flux density in the rotational ground state can also be obtained via eq 38 if the corresponding electronic probability density is known. Applications of this continuity equation 38 within the BOA to vibrating or dissociating diatomics in the rotational ground state are found in refs 3−6.

5. CONCLUSION

In the present work, the general expressions for the probability and flux densities of an arbitrary particle in the center-of-mass frame of a nonrelativistic closed many-body system without external interactions and without applying BOA are derived. Using the time-dependent wave function that consists of different exact stationary wave functions of this system,[10] it is shown that in the rotational ground state, in which the system has no predefined rotation axis, the time-dependent one-particle probability and flux densities in the center-of-mass frame are always isotropic; i.e., they have no angular dependence.

It is important to notice that the angular components of the one-particle flux density in the rotational ground state always vanish. One can expect that it is also applicable within the BOA, in which the electronic flux density for a single electronic state cannot be calculated directly by using the well-known formula for the flux density. But it can be obtained via the continuity equation for the rotational ground state thanks to the angular

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independence of the flux density in the center-of-mass frame. It enables the calculation of the electronic flux density instead of the electronic flux[2] in vibrating or dissociating molecules in the rotational ground state.[3−6]

The possible extension of the present work is the investigation of the symmetry properties of the probability and flux densities in excited rotational states ($J \neq 0$). Furthermore, one expects that in the rotational states with zero or nonzero magnetic quantum numbers ($M = 0$ or $M \neq 0$), there are zero or nonzero ring currents about the rotation axis of the system; i.e., the azimuthal component of the flux density in the center-of-mass frame is zero or nonzero, respectively. The angular dependencies should be similar to those of electronic and nuclear flux densities in atoms.[13,14] To investigate corresponding symmetry properties, one has to use analytical expressions for the inverse functions of eqs 25 and 28, i.e., $\Psi(\Psi',\Theta',\phi,\theta)$ and $\Theta(\Psi',\Theta',\phi,\theta)$, and the Wigner D-matrices[17] appearing in exact stationary wave functions.[10]

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