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1980 J. Phys. A: Math. Gen. 13 2287

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On body-fixed frames and angular momentum projection operators

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Received 8 October 1979

Abstract. Transformation to a body fixed reference frame and direct projection of angular momentum quantum numbers are alternative ways to account for rotational invariance of a many-body Hamiltonian. We illustrate both procedures by comparing the Born–Huang and the generator coordinate treatment of a diatomic system.

1. Introduction and definitions

Group theory provides a way to partially determine the eigenfunctions of a Hamiltonian operator from their transformation properties. Configuration space can always be divided into parts which result from a fundamental region by applying the elements of the symmetry group. If the wavefunction is known in the fundamental region, it is known everywhere. In particular, rotational invariance implies that the wavefunction is completely determined by its values at all interparticle distances, i.e. for all ‘shapes’ of the many-body system. Mathematically this is expressed through the transformation law of angular momentum eigenstates

$$\Psi_{JM}(x) = \sum_K D_{MK}^{J*}(\Omega) \Psi_{JK}(x'). \quad (1.1)$$

Here $D_{MK}^J(\Omega)$ are the Wigner D -functions of Euler angles Ω as defined in Edmonds’ standard textbook (Edmonds 1957) on angular momentum. In this context it is customary to adopt the passive point of view of rotations, i.e., x' are the coordinates of the particles in a rotated system of axes specified by the Euler angles Ω . The connection between the operator $\mathcal{R}_p(\Omega)$ transforming the original frame S into the rotated one S' and the coordinate change $x' = P(\Omega)x$ is as follows

$$\Psi(x') = \mathcal{R}_p^{-1}(\Omega) \Psi(x) = \Psi(P(\Omega)x) \quad (1.2)$$

$$\mathcal{R}_p(\Omega) = e^{i\gamma J_z} e^{i\beta J_y} e^{i\alpha J_z} \quad (1.3)$$

$$P(\Omega) = \begin{pmatrix} \cos \gamma \cos \beta \cos \alpha - \sin \gamma \sin \alpha & -\sin \gamma \cos \beta \cos \alpha - \cos \gamma \sin \alpha & \sin \beta \cos \alpha \\ \cos \gamma \cos \beta \sin \alpha + \sin \gamma \cos \alpha & -\sin \gamma \cos \beta \sin \alpha + \cos \gamma \cos \alpha & \sin \beta \sin \alpha \\ -\cos \gamma \sin \beta & \sin \gamma \sin \beta & \cos \beta \end{pmatrix} \quad (1.4)$$

where J is the total angular momentum of the system.

For an explicit derivation of these results and a clarification of some well hidden errors in textbooks on the subject we refer to Bouten (1969). Historically Wigner (1959) first demonstrated that the S' axes could be defined by putting three constraints on the particle coordinates. Hirshfelder and Wigner (1935) further pointed out that one could think of S' as being rigidly attached to the particle structure. In this way one was lead to the concept of the 'body-fixed frame' (BF-frame). It is then possible, at least in principle, to always separate rotational from other types of collective motion by transforming the Hamiltonian to the BF-frame and to factorise out the total angular momentum squared (Edmonds 1957)

$$J^2 = \left[-\frac{\partial^2}{\partial \beta^2} - \cot \beta \frac{\partial}{\partial \beta} - \frac{1}{\sin^2 \beta} \left(\frac{\partial^2}{\partial \alpha^2} + \frac{\partial^2}{\partial \gamma^2} \right) + \frac{2 \cos \beta}{\sin^2 \beta} \frac{\partial^2}{\partial \alpha \partial \gamma} \right]. \tag{1.5}$$

The above scheme is based on first using the transformation properties of the exact wavefunction and will have to be complemented with an approximate expansion of the 'internal' part of this function in a suitable basis set. An alternative way of working is obtained by interchanging these two steps, i.e., first expand the eigenstates and then project from these approximate forms functions with good angular momentum quantum numbers. This can be done by means of the so called angular momentum projection operators

$$P_{MK}^J = [(2J + 1)/8\pi^2] \int D_{MK}^{J*}(\Omega) \mathcal{R}_A(\Omega) d\Omega \tag{1.6}$$

which are superpositions of group elements with the corresponding irreducible representations as weight factors. Here one takes the active point of view for the rotation operators

$$\mathcal{R}_A(\Omega) = e^{-i\alpha J_z} e^{-i\beta J_y} e^{-i\gamma J_z} = \mathcal{R}_p^{-1}(\Omega) \tag{1.7}$$

because only then does there exist an isomorphism between the rotation operators about the different axes in space and the associated matrices transforming the coordinates (Wigner 1959). P_{MK}^J , which is an integral operator, projects from any function an eigenstate of J^2 and J_z with associated quantum numbers J and M respectively. Such a function will however be K dependent. Therefore the final states are written as superpositions

$$\Psi_{JM}(x) = \sum_K c_K \Phi_{JMK}(x) \tag{1.8}$$

$$\Phi_{JMK}(x) = P_{MK}^J \phi(x) = \frac{(2J + 1)}{8\pi^2} \int D_{MK}^{J*}(\Omega) \mathcal{R}_A(\Omega) \Phi(x) d\Omega$$

in which the coefficients c_K are determined variationally. Using the following properties of the P_{MK}^J

$$[H, P_{MK}^J] = 0, \quad (P_{MK}^J)^+ = P_{KM}^J, \quad P_{KM}^J P_{MK'}^J = P_{KK'}^J \tag{1.9}$$

the resulting secular equation reads

$$\sum_{K'} [H_{KK'}^J - E \Delta_{KK'}^J] c_{K'} = 0 \tag{1.10}$$

$$H_{KK'}^J = \langle \Phi | H P_{KK'}^J | \Phi \rangle \quad \Delta_{KK'}^J = \langle \Phi | P_{KK'}^J | \Phi \rangle. \tag{1.11}$$

Both methods outlined are of course formally equivalent if the expansions used are exact. In practice, however, their usefulness will depend upon how transforming the Hamiltonian under consideration compares with projecting angular momentum for the chosen basis states. We will illustrate the possible differences by working out the problem for a diatomic system.

2. Diatomic systems as an example

After separating off the centre of mass motion the Hamiltonian for a system of two nuclei with charges and masses (Z_1, M_1) , (Z_2, M_2) and a number of electrons can be written as

$$H = -(1/2\mu)\Delta_{\mathbf{R}} - \frac{1}{2} \sum_i \Delta_{\mathbf{r}_i} - (1/2\mu) \left(\sum_i \nabla_{\mathbf{r}_i} \right)^2 + (Z_1 Z_2 / R) \\ - Z_1 \sum_i (1/|r_i - \mathbf{R}_1|) - Z_2 \sum_i (1/|r_i - \mathbf{R}_2|) + \sum_{i < j} (1/|r_i - r_j|). \quad (2.1)$$

Here μ is the reduced mass $(M_1 M_2) / M$, \mathbf{r}_i the position of the i th electron measured from the centre of mass of the nuclei, \mathbf{R} the vector connecting the two nuclei and $\mathbf{R}_1 = -(M_2 \mathbf{R}) / M$, $\mathbf{R}_2 = +(M_1 \mathbf{R}) / M$ ($M = M_1 + M_2$). H commutes with the total angular momentum

$$\mathbf{J} = \mathbf{R} \times \mathbf{P} + \sum_i \mathbf{r}_i \times \mathbf{p}_i = \mathbf{L} + \mathbf{I} \quad (2.2)$$

which is the sum of a nuclear \mathbf{L} and an electronic \mathbf{I} contribution. From the above expression it is clear that H depends upon the internuclear vector \mathbf{R} (not on \mathbf{R}_1 and \mathbf{R}_2 separately) such that we can write Schrödinger's equation as

$$H(r, \mathbf{R}) \Psi_{JM}(r, \mathbf{R}) = E_J \Psi_{JM}(r, \mathbf{R}). \quad (2.3)$$

The Born–Oppenheimer (Born and Huang 1954) and adiabatic approximations have made it customary to decompose H as the sum of the kinetic energy of the nuclear relative motion and the so called electronic Hamiltonian

$$H(r, \mathbf{R}) = -(1/2\mu)\Delta_{\mathbf{R}} + H_e(r, \mathbf{R}) \quad (2.4)$$

As an operator acting on the space of functions square integrable in the electron coordinates H_e is clearly invariant under rotations about \mathbf{R} and reflexions through planes containing \mathbf{R} . Therefore the solutions to the electronic Schrödinger equation can be labelled as follows (Landau and Lifshitz 1964)

$$H_e(r, \mathbf{R}) \varphi_{n\Lambda}(r|\mathbf{R}) = U_{n\Lambda}(\mathbf{R}) \varphi_{n\Lambda}(r|\mathbf{R}). \quad (2.5)$$

Here Λ denotes the absolute value of the electronic angular momentum along the internuclear axis, i.e. $\mathbf{I} \cdot \mathbf{R} / R$, while n stands for all other quantum numbers. The fact that H_e commutes with \mathbf{R} itself is demonstrated by the parametric dependence of the electronic eigenvalues and eigenfunctions upon this quantity. This is stressed by separating the dynamical coordinates r from the parameters \mathbf{R} by a vertical bar in the electronic eigenstates. By writing $U_{n\Lambda} = U_{n\Lambda}(\mathbf{R})$ we have anticipated the well known result (to be derived later) that the electronic eigenvalues depend upon the relative distance between nuclei only.

Before going any further one should notice that in writing down the Hamiltonian as in (2.1) we have neglected relativistic effects and assumed the coupling between the electron spin and orbital angular momenta to be negligible.

2.1. A BF-frame in the Born-Huang series

A convenient definition of the rotating reference frame for a diatomic system is to choose the z' -axis along the internuclear vector, i.e., the Euler angles α, β are taken as the polar angles $\omega_R = (\varphi_R, \theta_R)$ of \mathbf{R} . This corresponds to always taking y' perpendicular to the z, z' plane (Goodisman 1973). The transformation law (1.1) then takes the form ($\Omega = (\varphi_R, \theta_R, 0)$)

$$\begin{aligned}\Psi_{JM}(r, \mathbf{R}) &= \sum_{\Lambda} D_{M\Lambda}^{J*}(\varphi_R, \theta_R, 0) \Psi_{J\Lambda}(r', \mathbf{R}e_{z'}) \\ &\equiv \sum_{\Lambda} D_{M\Lambda}^{J*}(\omega_R) \Psi_{J\Lambda}(r'|R).\end{aligned}\quad (2.6)$$

The new electron coordinates are functions of the polar angles of \mathbf{R} , i.e., $r' = r'(\omega_R)$. The transformation of a position vector r_i to r'_i is given by (1.4) putting $(\alpha, \beta, \gamma) = (\varphi_R, \theta_R, 0)$. Clearly one has

$$(\mathbf{J} \cdot \mathbf{R})/R = J_{z'} = l_{z'} = (\mathbf{I} \cdot \mathbf{R})/R \quad (2.7)$$

i.e., there is no nuclear angular momentum about the body fixed axis. We have therefore used the notation Λ , common for the electronic angular momentum $l_{z'}$, to specify the $J_{z'}$ components in (2.6).

An appropriate basis to expand the $\Psi_{J\Lambda}(r'|R)$ are the electronic states $\varphi_{n\Lambda}(r'|R)$ defined in the BF-frame. For each Λ and R they form a complete set such that the full wavefunction takes the form

$$\Psi_{JM}(r, \mathbf{R}) = \sum_{n\Lambda} g_{n\Lambda}^J(\mathbf{R}) D_{M\Lambda}^{J*}(\omega_R) \varphi_{n\Lambda}(r'|R) \quad (2.8)$$

in which the radial functions $g_{n\Lambda}^J(\mathbf{R})$ remain to be determined. Each term in this expansion is a so called adiabatic wavefunction. Summation of the electronic quantum numbers gives the Born-Huang (BH) series (2.8) (Born and Huang 1954).

On substituting (2.8) into Schrödinger's equation one must take into account the implicit dependence of the electron coordinates on the polar angles ω_R . This means that differentiations with respect to φ_R and θ_R are to be replaced by

$$\frac{\partial}{\partial \theta_R} + \sum_i \frac{\partial x'_i}{\partial \theta_R} \frac{\partial}{\partial x'_i} + \dots = \frac{\partial}{\partial \theta_R} - i l_{y'} \quad (2.9a)$$

$$\frac{\partial}{\partial \varphi_R} + \sum_i \frac{\partial x'_i}{\partial \varphi_R} \frac{\partial}{\partial x'_i} + \dots = \frac{\partial}{\partial \varphi_R} - i \cos \theta_R l_{z'} + i \sin \theta_R l_{x'} \quad (2.9b)$$

where the partial derivatives indicate differentiation with respect to explicit occurrence of θ_R and φ_R . Making this substitution amounts to transforming the Hamiltonian from the space-fixed (SF-frame) to the BF-frame. The extra terms arising from the nuclear kinetic energy can be combined to give the total angular momentum squared ($\Delta(\omega_R)$ is the angular part of $\Delta_{\mathbf{R}}$)

$$J^2 = -\left(\Delta(\omega_R) - 2i \frac{\cot \theta_R}{\sin \theta_R} l_{z'} \frac{\partial}{\partial \varphi_R} - \frac{1}{\sin^2 \theta_R} l_{z'}^2 \right) \quad (2.10)$$

and a number of coupling terms. Expression (2.10) can easily be checked from (1.5) noticing that in this case $(\varphi_R, \theta_R) = (\alpha, \beta)$ and $l_z = -i \partial/\partial\gamma$. Substitution of (2.8) into the transformed Schrödinger equation then gives a set of coupled differential equations for the radial functions $g_{n\Lambda}^J(\mathbf{R})$

$$\left(-\frac{1}{2\mu} \frac{d^2}{dR^2} + \frac{J(J+1) - \Lambda^2}{2\mu R^2} + U_{n\Lambda}(\mathbf{R})\right)(\mathbf{R}g_{n\Lambda}^J(\mathbf{R})) = -\sum_{n'\Lambda'} C_{n\Lambda, n'\Lambda'}^J\left(\mathbf{R}, \frac{d}{d\mathbf{R}}\right)(\mathbf{R}g_{n'\Lambda'}^J(\mathbf{R})). \quad (2.11)$$

The coupling terms contained in $C_{n\Lambda, n'\Lambda'}^J$ are proportional to matrix elements of following form

$$\left\langle \varphi_{n\Lambda}(\mathbf{R}) \left| \frac{d}{d\mathbf{R}} \right| \varphi_{n'\Lambda}(\mathbf{R}) \right\rangle \frac{d}{d\mathbf{R}} \quad \left\langle \varphi_{n\Lambda}(\mathbf{R}) \left| \frac{d^2}{dR^2} \right| \varphi_{n'\Lambda}(\mathbf{R}) \right\rangle \quad (2.12a)$$

$$\langle \varphi_{n\Lambda}(\mathbf{R}) | l_{\pm}' | \varphi_{n'\Lambda \pm 1}(\mathbf{R}) \rangle \quad \langle \varphi_{n\Lambda}(\mathbf{R}) | l_x'^2 + l_y'^2 | \varphi_{n'\Lambda}(\mathbf{R}) \rangle. \quad (2.12b)$$

The two groups are referred to as radial and angular couplings respectively. The explicit expression for the full set of equations is rather lengthy and will not be given here. It can be found in Redmon (1974) and Van Vleck (1951).

2.2. Angular momentum projection operators in the generator coordinate expansion

Recently an alternative to the Born-Huang approach, based on the generator coordinate theory of molecules, was suggested (Lathouwers 1979). The generator coordinate form of the wavefunction is an expansion in terms of basis functions $\chi_{n\Lambda}(\mathbf{r}, \mathbf{R}|\alpha) = \varphi_{n\Lambda}(\mathbf{r}|\alpha)\Phi(|\mathbf{R}-\alpha|)$ which are products of an electronic and a nuclear part. The $\varphi_{n\Lambda}(\mathbf{r}|\alpha)$ are the eigenstates of the electronic Hamiltonian $H_e(\alpha) \equiv H_e(\mathbf{R} = \alpha)$ whereas the function $\Phi(|\mathbf{R}-\alpha|)$ strongly localises the nuclei around a position specified by the vector α , i.e., $\Phi(|\mathbf{R}-\alpha|)$ is significantly different from zero only if $|\mathbf{R}-\alpha| = 0$. One can therefore say that the basis products $\chi_{n\Lambda}$ describe electrons moving in the force field determined by the most probable positions of the nuclei. The wavefunction is now generated as a superposition of the $\chi_{n\Lambda}(\mathbf{r}, \mathbf{R}|\alpha)$ by summing over the electronic quantum numbers $n\Lambda$ and integrating over the vector α

$$\Psi(\mathbf{r}, \mathbf{R}) = \sum_{n\Lambda} \int F_{n\Lambda}(\alpha) \varphi_{n\Lambda}(\mathbf{r}|\alpha) \Phi(|\mathbf{R}-\alpha|) d\alpha \quad (2.13)$$

where the $F_{n\Lambda}(\alpha)$ are the expansion coefficients. The components of α are generally referred to as generator coordinates because they appear as extra variables serving only to label the basis states and generate the wavefunction through integration. In this process, however, they disappear from the final result $\Psi(\mathbf{r}, \mathbf{R})$. For further details on the GCM we refer to Lathouwers (1978). What interests us here is that (2.13) is an exact representation of the wavefunction Lathouwers (1979) such that the variational principle applied to the weight functions $F_{n\Lambda}(\alpha)$ will automatically lead to angular momentum eigenstates. The question is whether one can also determine part of the $F_{n\Lambda}(\alpha)$ from first principles by analogy with the separation of the Wigner D -functions (1.1).

For this purpose we will use the following property of the electronic Hamiltonian: the parametric dependence of H_e on the generating vector α is such that

$$H_e(\alpha) = \mathcal{R}_e(\omega_\alpha) H_e(\alpha \mathbf{e}_z) \mathcal{R}_e^{-1}(\omega_\alpha) \quad (2.14)$$

where e_z is the space fixed z -axis and $\mathcal{R}_e(\omega_\alpha)$ the (active) rotation operator in the electron space. This relation is a direct consequence of the fact that Coulomb interactions depend upon the mutual distance between the particles only. Equation (2.14) states that $H_e(\alpha)$ and $H_e(\alpha e_z)$ are unitary equivalent. This implies that the spectra of these operators are identical, i.e., $U_{n\Lambda} = U_{n\Lambda}(\alpha) = U_{n\Lambda}(\alpha e_z)$, a result we used earlier (2.5). Furthermore the associated eigenfunctions are transformed into each other through the unitary operator $\mathcal{R}_e(\omega_\alpha)$, i.e.,

$$\varphi_{n\Lambda}(r|\alpha) = \mathcal{R}_e(\omega_\alpha)\varphi_{n\Lambda}(r|\alpha e_z). \quad (2.15)$$

As for the nuclear part of the basis functions it is clear that

$$\Phi(|\mathbf{R} - \alpha|) = \mathcal{R}_n(\omega_\alpha)\Phi(|\mathbf{R} - \alpha e_z|) \quad (2.16)$$

$\mathcal{R}_n(\omega_\alpha)$ indicating the rotation operator in nuclear space. Combining (2.15) and (2.16) we can state that for the full intrinsic states one has

$$\chi_{n\Lambda}(r, \mathbf{R}|\alpha) = \mathcal{R}(\omega_\alpha)\chi_{n\Lambda}(r, \mathbf{R}|\alpha e_z). \quad (2.17)$$

It is also easily seen that $\chi_{n\Lambda}(\alpha e_z)$ is an eigenstate of J_z with eigenvalue Λ

$$J_z\chi_{n\Lambda}(\alpha e_z) = \Lambda\chi_{n\Lambda}(\alpha e_z). \quad (2.18)$$

The last two equations can now be used to partially determine the weight function $F_{n\Lambda}(\alpha)$. Using (2.17) we can write (2.13) as

$$\Psi(r, \mathbf{R}) = \sum_{n\Lambda} \int F_{n\Lambda}(\alpha) \mathcal{R}(\omega_\alpha)\chi_{n\Lambda}(r, \mathbf{R}|\alpha e_z) d\alpha. \quad (2.19)$$

In this expression one starts to recognise the form of the angular momentum projection operators (1.6). Firstly, one can easily build in the third, redundant, Euler angle, say γ_α , by inserting $e^{i\gamma_\alpha\Lambda} e^{-i\gamma_\alpha J_z}$ in front of $\chi_{n\Lambda}(\alpha e_z)$. Secondly, knowing that P_{MK}^J working on an eigenfunction of J_z will give zero unless the associated eigenvalue equals K and taking into account the variational procedure (1.8)–(1.11) the angular dependence of the weight functions must be such that

$$F_{n\Lambda}^{JM}(\alpha) = f_{n\Lambda}^J(\alpha) D_{M\Lambda}^{J*}(\omega_\alpha). \quad (2.20)$$

With this choice the GCM wavefunctions will be the angular momentum eigenstates

$$\begin{aligned} \Psi_{JM}(r, \mathbf{R}) &= \sum_{n\Lambda} \int f_{n\Lambda}^J(\alpha) D_{M\Lambda}^{J*}(\omega_\alpha)\chi_{n\Lambda}(r, \mathbf{R}|\alpha) d\alpha \\ &= \sum_{n\Lambda} \int f_{n\Lambda}^J(\alpha) D_{M\Lambda}^{J*}(\Omega_\alpha)\mathcal{R}(\Omega_\alpha)\chi_{n\Lambda}(r, \mathbf{R}|\alpha e_z) d\alpha \\ &= \sum_{n\Lambda} \int f_{n\Lambda}^J(\alpha) P_{M\Lambda}^J\chi_{n\Lambda}(r, \mathbf{R}|\alpha e_z)\alpha^2 d\alpha. \end{aligned} \quad (2.21)$$

The optimal radial weight functions obey a set of coupled integral equations (Lathouwers 1979) which can be derived using (2.21) and the projection operator

properties (1.9).

$$\int K_{n\Lambda, n\Lambda}^J(\alpha, \beta|E) f_{n\Lambda}^J(\beta) \beta^2 d\beta = - \sum_{n'\Lambda'} \int K_{n\Lambda, n'\Lambda'}^J(\alpha, \beta|E) f_{n'\Lambda'}^J(\beta) \beta^2 d\beta \quad (2.22)$$

$$K_{n\Lambda, n'\Lambda'}^J(\alpha, \beta|E) = H_{n\Lambda, n'\Lambda'}^J(\alpha, \beta) - E \Delta_{n\Lambda, n'\Lambda'}^J(\alpha, \beta) \quad (2.23)$$

$$H_{n\Lambda, n'\Lambda'}^J(\alpha, \beta) = \langle \chi_{n\Lambda}(\alpha \mathbf{e}_z) | HP_{\Lambda\Lambda'}^J | \chi_{n'\Lambda'}(\beta \mathbf{e}_z) \rangle \quad (2.24)$$

$$\Delta_{n\Lambda, n'\Lambda'}^J(\alpha, \beta) = \langle \chi_{n\Lambda}(\alpha \mathbf{e}_z) | P_{\Lambda\Lambda'}^J | \chi_{n'\Lambda'}(\beta \mathbf{e}_z) \rangle.$$

The expressions for the kernels can be further simplified inserting the explicit form of the projection operators and using properties (2.17) and (2.18) of the intrinsic states. For example, the most complicated matrix elements to be calculated here, i.e., the Hamiltonian couplings $H_{n\Lambda, n'\Lambda'}^J$, become

$$\begin{aligned} H_{n\Lambda, n'\Lambda'}^J(\alpha, \beta) &= \int d \cos \theta d_{\Lambda\Lambda'}^J(\theta) \langle \chi_{n\Lambda}(\alpha \mathbf{e}_z) | H e^{-i\theta J_y} | \chi_{n'\Lambda'}(\beta \mathbf{e}_z) \rangle \\ &= \int d \cos \theta d_{\Lambda\Lambda'}^J(\cos \theta) \langle \chi_{n\Lambda}(\alpha \mathbf{e}_z) | H | \chi_{n'\Lambda'}(\beta \cos \theta \mathbf{e}_z + \beta \sin \theta \mathbf{e}_x) \rangle. \end{aligned} \quad (2.25)$$

3. Discussion and generalisations

Before discussing the differences between the above two approaches we will emphasise their interrelationship. The generator coordinate functions in (2.21) are constructed in such a way that they give the corresponding adiabatic ones if one fixes the nuclei in the intrinsic states, i.e., if one sets $\Phi(|\mathbf{R} - \alpha|) = \delta(\mathbf{R} - \alpha)$. This implies that all GCM quantities, such as energies and weight functions, will go over into their adiabatic counterparts, eigenvalues of adiabatic differential equations and nuclear wavefunctions, if one makes the substitution $\Phi = \delta$. In particular (2.13) becomes

$$\Psi(r, \mathbf{R}) = \sum_{n\Lambda} F_{n\Lambda}(\mathbf{R}) \varphi_{n\Lambda}(r|\mathbf{R}) \quad (3.1)$$

which is an expansion in space-fixed electronic states. From the GCM treatment of total angular momentum it follows that if (3.1) is to be an eigenstate $\Psi_{JM}(r, \mathbf{R})$ of J^2 and J_z one must have

$$F_{n\Lambda}^{JM}(\mathbf{R}) = f_{n\Lambda}^J(\mathbf{R}) D_{M\Lambda}^{J*}(\omega_{\mathbf{R}}). \quad (3.2)$$

On the other hand using the transformation law (1.1) on (3.1) one obtains

$$\Psi_{JM}(r, \mathbf{R}) = \sum_{\Lambda'} D_{M\Lambda'}^{J*}(\omega_{\mathbf{R}}) \sum_{n\Lambda} F_{n\Lambda}^{J\Lambda'}(\mathbf{R}, \omega_{\mathbf{R}} = 0) \varphi_{n\Lambda}(r'|\mathbf{R}). \quad (3.3)$$

While it is clear from (3.2) that

$$\begin{aligned} F_{n\Lambda}^{J\Lambda'}(\mathbf{R}, \omega_{\mathbf{R}} = 0) &= f_{n\Lambda}^J(\mathbf{R}) d_{\Lambda'\Lambda}^J(0) \\ &= f_{n\Lambda}^J(\mathbf{R}) \delta_{\Lambda'\Lambda}. \end{aligned} \quad (3.4)$$

Combining the last two expressions gives the BH expansion of the wavefunction (2.8) in the BF-frame version. This elementary arithmetic shows that

$$\lim_{\Phi \rightarrow \delta} f_{n\Lambda}^J = g_{n\Lambda}^J, \quad (3.5)$$

i.e., in the delta function limit the GCM weight functions, and consequently each of the individual terms in the GCM expansion, are transformed into the adiabatic nuclear wavefunctions and the associated terms in the BH series.

We will discuss the differences between the two schemes used by means of table 1 in which consecutive steps in the process of arriving at the final equations are compared. Each of the following paragraphs treats one point of comparison.

Table 1.

	Born-Huang expansion	Generator coordinate expansion
Technique used to obtain angular momentum eigenstates	Transformation to the BF-frame	Introduction of angular momentum projection operators
Type of rotation operators	Passive	Active
Resulting type of equations	Coupled differential equations	Coupled integral equations
Origin of coupling terms	Coupling of electronic states by the nuclear kinetic energy in the BF-frame	Coupling of JM projections from different intrinsic states by the SF Hamiltonian
Form of the coupling terms	Matrix elements of first and second-order differential operators with respect to electronic states in BF-frame	Integrals of Wigner d -functions and matrix elements of the SF Hamiltonian with respect to intrinsic states

In the Born-Huang expansion the transformation to the BF-frame is the starting point. Afterwards an expansion of the internal wavefunction is introduced. In the GCM, however, a space-fixed expansion is introduced first, after which rotational symmetry is treated in the space of GC's via angular momentum projection operators. This interchange between a technique to conserve total angular momentum and the use of a basis set implies that in the Born-Huang approach a transformation to the BF-frame is necessary while in the GCM the original space-fixed Hamiltonian can be used.

A further implication of the above mentioned switch is the type of rotation operators appearing in the respective formulations. Obviously the body-fixed or rotating system of axes leads to the passive point of view. In the GCM, however, the wavefunctions are superpositions of basis states associated with different orientations of the GC vector. It is then more natural to adopt the active point of view and to look upon the intrinsic states $\chi_{n\Lambda}(\alpha)$ as active rotations of the basis functions $\chi_{n\Lambda}(\alpha e_z)$. Because of the existing isomorphism between active rotation operators and the associated coordinate transformations and the fact that it is easier to visualise the actual rotational motion of the many-body system through the basis functions, we find it didactically appealing to use the GC approach.

Comparing the coupled equations (2.11) and (2.22) one notices that the potential energy curves and coupling potentials have been replaced by integral kernels. In general one can say that integral equations give a more global picture than the pointwise evolution implied by differential operators. As for the computation of the quantities entering the coupled equations the evaluation of the matrix elements (2.12a–b) have been discussed in detail in the literature (Browne 1972). The main complications arising are the derivatives with respect to R of the electronic states, since the latter may depend upon internuclear distance in various ways (orbital exponents, orbital centres, and expansion coefficients). For an easy computation of the GC kernels one must keep two things in mind. Firstly, it is preferable to use the same type of one-particle basis functions for electrons and nuclei (e.g. Gaussians) since this will lead to well known multicentre integrals. Secondly if one wants to compute everything in a space-fixed frame it must be possible to replace the effect of rotation operators by an equivalent transformation in the GC space, i.e., intrinsic states are to be constructed such that (2.17) holds.

It is clear that the Born–Huang couplings (2.12a–b) vanish unless $\Delta\Lambda = 0, \pm 1$. In the GCM the coupling between two electronic states Λ_1 and Λ_2 is governed by matrix elements of $P_{\Lambda_1\Lambda_2}^J$. This means that in the GCM one can have an idea of the (Λ_1, Λ_2) interaction strength by estimating the size of these integrals whereas in the Born–Huang approach a solution of the equations linking Λ_1 , and Λ_2 is the only way to find out the importance of the coupling between these states. The separation in radial ($\Delta\Lambda = 0$) and angular ($\Delta\Lambda = \pm 1$) couplings does not appear in the GCM. It should also be noticed that when a diabatic basis (Smith 1969) is used, the form of the GCM equation is unmodified. In contrast, different and (or) additional coupling terms arise if diabatic states are used in the BH series.

In the polyatomic case the most popular choice for the BF-axis is the so called Eckart (1930) frame. This set of axes is convenient to separate the rotational and vibrational motion of the system by approximating it by a semi-rigid rotor and by introducing normal vibrational coordinates. However, the explicit transformation of the molecular Hamiltonian to the Eckardt frame becomes prohibitively complicated. A workable set of coupled differential equations for the general polyatomic case has, to our knowledge, never been given. In the GCM the situation is more favourable. Indeed, electronic Hamiltonians for differently oriented nuclear skeletons are, as in the diatomic case, unitary equivalent. If one then constructs the nuclear basis functions from one-particle functions $\Phi(|\mathbf{R}_i - \boldsymbol{\alpha}_i|)$, properly taking account of nuclear statistics, one obtains intrinsic states for which rotations in Hilbert space can be replaced by GC transformations. This means that the projection techniques can be used without further ado. The only complication arising is that since the intrinsic states will no longer be eigenstates of J_z , generation of matrix elements will involve three Euler angles and the full set of coefficients c_k will have to be determined variationally. Thus, in the GCM the total angular momentum of a polyatomic system can be conserved at the cost of three-dimensional integrals over Euler angles and the solution of a $(2J + 1)$ -dimensional secular equation.

The use of BF or SF frames, in molecular scattering problems, has been discussed extensively (for a review see Choi *et al* (1978)). In general one can say that the derivation of cross-sections is more tractable in the BF formulation, whereas matching the asymptotic boundary conditions is easier in a SF approach (Pack 1973). The GCM has been extended to include scattering situations Lathouwers (1979) and a separate paper will be devoted to its treatment of atom–atom collisions.

Acknowledgments

This work was sponsored by the NATO grant no. 1776 and the IIKW (Interuniversitair Instituut voor Kernwetenschappen), Belgium. The author would like to thank Professor P Van Leuven for many interesting discussions.

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