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Generator-coordinate theory of molecular spectra

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We review the merits and shortcomings of the Born-Oppenheimer separation and suggest a nonadiabatic approach to molecular spectra using the generator-coordinate method. The adiabatic approximation and the new scheme are worked out in parallel for diatomic molecules.

I. INTRODUCTION

The Born-Oppenheimer (BO) separation is undoubtedly one of the cornerstones of theoretical molecular and solid-state physics. It has become so familiar that we actually think of a molecule as some semirigid nuclear frame supporting an electronic cloud. Apart from separating motions of light and heavy particles, the BO paper[1] has had the remarkable side effect of splitting physicists and chemists into "theoreticians" and "experimentalists." The former (e.g., quantum chemists) are mainly interested in the computation of potential-energy surfaces of electronic Hamiltonians, whereas the latter (e.g., spectroscopists) try to explain observations in terms of parametrized potentials. While, in the course of more than 50 years of quantum mechanics, a vast technology for treating problems in both fields has been developed, the interaction between them has been disappointingly small. The reason, apparently, is that so far one has not succeeded in going beyond the BO approximation for reasonable sized systems while the most accurately calculated potential-energy surfaces can still not compete with sufficiently sophisticated parametrized forms. However, if one accepts that Schrödinger's equation gives an accurate description of molecules and solids the ultimate goal should be to solve it using quantum mechanics alone rather than to rely upon a semiclassical model such as the BO scheme.[2] In view of the growth of computer facilities over the last decades, this would be possible if one could only force oneself to picture a molecule as an assembly of quantum-mechanical particles instead of as a system with a double nature. The present paper is an attempt in this direction.

II. ADIABATIC APPROXIMATION AND THE GENERATOR COORDINATE METHOD

A. Basic ideas

In their original treatment Born and Oppenheimer[1] expanded the total Hamiltonian around some nuclear configuration R_0. The eigenvalue problem was then solved by the usual methods of perturbation theory (PT). It turns out that the appropriate coupling constant is $\kappa=(m/M)^{1/4}$, where m and M are the electron and proton mass, respectively. Up to second order, the nuclear part of the wave function (wf) can be obtained applying PT to a differential equation with an effective potential including fourth powers of nuclear displacements. By adding higher-order terms to the final-state vector, it can be written as a product of an electronic and a nuclear function. However, if one proceeds even further (κ^3 in the wf and κ^5 in energy) the dynamics of the nuclei can no longer be described on the basis of an average potential and the product form of the state vectors is lost.[3]

Rather than continue along these lines, which becomes tedious anyway,[3] one can postulate the product form of the wf from the outset and justify it by physical intuition. In view of the large mass difference $m \ll M$, one assumes that the nuclei move much slower than the electrons such that the latter see the heavy particles essentially as fixed force centers. Considering the nuclei as classical point masses, describing certain time-dependent paths $R=R(t)$, one can then introduce the adiabatic approximation[4] which consists of assuming that the electronic quantum numbers will not change during this motion. The electronic state will adapt itself instantaneously to a displacement of the nuclei. In order to obtain the nuclear part of the wf one thereafter considers the heavy particles as quantum-mechanical objects, subject to the average effect of the quickly revolving electrons. Their role is to create an effective potential for the nuclear motion.

The above scheme, commonly referred to as the adiabatic approximation (AA) makes the approximate solution of the many-body Schrödinger equation a more feasible task. However, this is achieved at the cost of mutilating classical and quantum mechanics. The nuclei play a dual role, classical in the eyes of the electrons but quantal if interacting between themselves and with the electronic cloud. The adiabatic approximation can therefore be classified as a "semiclassical" theory. This statement has been strongly emphasized by Woolley and Sutcliffe.[5] They pointed out that most of the primary concepts used in molecular spectroscopy, traditionally attributed to the AA, were developed within the framework of the old quantum theory. Examples are, the potential-energy surfaces,[6] the separation of the molecular energies into electronic, vibrational and rotational contributions,[7] the symmetry classification of electronic levels in diatomics,[8] etc. The close relationship between the AA and semiclassical approaches is further demonstrated by the Rydberg-Klein-Rees procedure for constructing potential-energy curves.[8] This technique based on the Bohr-Sommerfeld quantization rule is superior to more quantal methods (e.g., fitting spectroscopic constants in PT expressions for truncated power series expansions of potential-energy surfaces). Term values can be reproduced differing from the experimental values by less than the magnitude of the so-called nonadiabatic corrections.[9] Clearly, this is pushing the model beyond its limits since the exact electronic eigenvalue will not give that kind of accuracy. Situations like these together with more arguments given in Ref. (5) express the desirability of constructing a theory free of semiclassical contamination (see also Refs. 10–14).

Several attempts have been made to go beyond the AA (for a review see Ref. 15). However, none of them seems to be feasible for more than two electron diatomics. The most general approach is the one suggested by Born[16] based on an expansion of the wf in terms of the complete set of electronic eigenstates. The coefficients, which are functions of the nuclear coordinates, must then obey an infinite set of coupled differential equations. This method, although formally exact, is of little practical use. Indeed the application to H_2^+ has shown that the Born series, the first term of which represents the adiabatic wf, is very slowly convergent.[15] This means that a large number of electronic states have to be known at all internuclear distances. In addition one should include the electronic continua contributions which leads to a set of coupled integrodifferential equations. Thus the Born method, although useful for a general discussion, is certainly not at present feasible for many-electron diatomic or polyatomic molecules. Instead of trying to increase the accuracy of the AA, it seems more reasonable to drop the idea of separating electronic and nuclear motions from the very beginning. However, at the same time one should be careful not to lose the simplifying features of the adiabatic approach (e.g., the separation of the energy in its electronic, vibrational, and rotational parts). It will also be advisable to make optimal use of the results already available for the electronic eigenvalue problem.

An outline for constructing a theory fulfilling the above requirements has recently been given.[17] Inspiration was found in nuclear physics, more precisely from the description of collective motion in nuclei. Here an alternative to the classical Bohr-Mottelson approach[18] was suggested by Griffin, Hill, and Wheeler.[19,20] They considered trial functions of the form

$$\Psi(x)=\int f(\alpha)\chi(x\,|\,\alpha)\,d\alpha\,,$$

where x stands for all particle degrees of freedom and α denotes a set of parameters related to the collective motion. The wf's $\Psi(x)$ are linear superpositions of continuously labelled basis states $\chi(x\,|\,\alpha)$, frequently termed "intrinsic states", with weight functions $f(\alpha)$. If the latter are determined from the variational principle they must satisfy the secular equation

$$\int[H(\alpha,\beta)-E\,\Delta(\alpha,\beta)]f(\beta)\,d\beta=0\,,$$

$$H(\alpha,\beta)=\langle\chi(\alpha)\,|H|\,\chi(\beta)\rangle\,,$$

$$\Delta(\alpha,\beta)=\langle\chi(\alpha)\,|\,\chi(\beta)\rangle\,.$$

The above integral equation, supplemented with a boundary condition, is known as the Griffin-Hill-Wheeler (GHW) eigenvalue problem. Its eigenvalues are upper bounds to the exact energies of H. The success of the method depends critically upon the way the parameters α are built into the intrinsic states. However by integrating over the α range the parameters are no longer present in the final result. They appear as extra coordinates which serve only to label the basis states and generate the wf's. Hence the name of the above variational procedure: generator coordinate method (GCM). In the following sections we will show that the AA can be formulated as a generator coordinate method in which "molecular structures" play the generator coordinate part. This then suggests a more quantal treatment of the nuclei which results in a nonproduct type of wf. The theory is applied in detail to diatomics.

B. Trial functions

The molecular Hamiltonian is the sum of three terms

$$H=T+t+V\,, \tag{2.1}$$

where T and t are the nuclear and electronic kinetic-energy operators and V contains the Coulomb interaction between all particles. In the limit of infinite nuclear masses we have

$$H_0 = \lim_{M\to\infty} H = t + V , \qquad (2.2)$$

where H_0 is the electronic Hamiltonian. In order for H_0 to be a meaningful operator on the Hilbert space of the electrons one has to specify the nuclear positions. We denote a nuclear configuration by a set of values α. Since H_0 does not contain any derivatives with respect to α it follows that

$$[H_0, \alpha] = 0. \qquad (2.3)$$

Hence the values α are good quantum numbers for the electronic eigenvalue problem corresponding to $H_0(\alpha)$, i.e.,

$$H_0(\alpha)\varphi_n(r\,|\,\alpha) = U_n(\alpha)\varphi_n(r\,|\,\alpha), \qquad (2.4)$$

where n stands for the electronic state labels other than α. Thus for nuclei at α, the $\{r, R\}$ representation of the molecular wf is

$$\varphi_n(r\,|\,\alpha)\delta(R-\alpha). \qquad (2.5)$$

These are the so-called fixed nuclei states. They depend parametrically on the nuclear positions. In the adiabatic approximation, i.e., under the assumption that the n are good quantum numbers for the total molecular state, the most general trial functions one can form are linear combinations of (2.5) for different α values[21]

$$\Psi^{\mathrm{AD}}(r,R) = \int f(\alpha)\varphi_n(r\,|\,\alpha)\delta(R-\alpha)\,d\alpha$$
$$= \varphi_n(r\,|\,R)f(R). \qquad (2.6)$$

The explicit integration over the nuclear structures gives the usual product form. The important result here is that the intermediate integral form of Ψ^{AD} shows that the AA is equivalent to a generator coordinate procedure using fixed nuclei intrinsic states (2.5).

An obvious way to generalize Ψ^{AD} if considered as a product is to add extra terms. This can be done systematically by writing down the Born expansion

$$\Psi^{\mathrm{B}}(r,R) = \varphi_n(r\,|\,R)f(R) + \sum_{m\neq n} \varphi_m(r\,|\,R)f_m(R), \qquad (2.7)$$

where $\sum$ stands for summation over the discrete and integration over the continuous part of the spectrum. The GCM form of Ψ^{AD}, however, offers a more direct way to introduce nonadiabaticity. Indeed, in view of the fact that $M\neq\infty$, it seems reasonable to replace the delta distribution $\delta(R-\alpha)$ by a function $\Phi(R\,|\,\alpha)$ which is sharply peaked around α, i.e., we suggest

$$\Psi^{\mathrm{GCM}}(r,R) = \int f(\alpha)\varphi_n(r\,|\,\alpha)\Phi(R\,|\,\alpha)\,d\alpha. \qquad (2.8)$$

Because of the finite extension in space of $\Phi(R\,|\,\alpha)$ the integration over the nuclear configurations now generates nonproduct trial functions from product type intrinsic states

$$\chi_n(r,R\,|\,\alpha) = \varphi_n(r\,|\,\alpha)\Phi(R\,|\,\alpha). \qquad (2.9)$$

The maxima in the electronic and nuclear part both occur at α such that these basis functions describe electrons moving in the average (rather than instantaneous) field of the nuclei. By superimposing them we conserve the adiabatic hypothesis, i.e., the electronic quantum numbers are kept constant. However, nonadiabaticity is introduced by modifying the nuclear basis states and integrating out the "molecular structures" α which play an intermediate role only.

Whereas the AA is represented by the first term in the Born expansion, the transition from the GCM to the AA can be carried out by narrowing $\Phi(R\,|\,\alpha)$ to a δ distribution, i.e.,

$$\Psi^{\mathrm{AD}}(r,R) = \lim_{\Phi\to\delta} \Psi^{\mathrm{GCM}}(r,R). \qquad (2.10)$$

Thus, the GCM goes over into the AA by fixing the nuclei in the intrinsic states. Both the Born and GCM approach contain the AA as a special case the difference lies in the way nonadiabatic effects are introduced. In view of the slow convergence of (2.7) use of this expansion requires knowledge of a large number of electronic states. In the GCM replacing $\delta(R-\alpha)$ by $\Phi(R\,|\,\alpha)$ couples electron and nuclear motion directly.

C. Variational equations

The variational principle applied to the product form of the adiabatic trial functions leads to the well-known "Schrödinger equation" for the nuclear motion

$$[T + U_n(R) + C_n(R)]f^{\mathrm{AD}}(R) = Ef^{\mathrm{AD}}(R), \qquad (2.11)$$

where $C_n(R) = \langle\varphi_n(R)\,|\,T\,|\,\varphi_n(R)\rangle$ is the so-called adiabatic correction term to the fixed nucleus potential $U_n(R)$. One can just as well apply the GC variational principle to the weight function $f^{\mathrm{AD}}(\alpha)$. This gives a GHW integral equation with kernels

$$\Delta_n^{\mathrm{AD}}(\alpha,\beta) = \langle\varphi_n(\alpha)\,|\,\varphi_n(\beta)\rangle\delta(\alpha-\beta),$$
$$H_n^{\mathrm{AD}}(\alpha,\beta) = \langle\varphi_n(\alpha)\,|\,\varphi_n(\beta)\rangle T(\alpha)\delta(\alpha-\beta) \qquad (2.12)$$
$$+ U_n[\tfrac{1}{2}(\alpha+\beta)]\,\Delta^{\mathrm{AD}}(\alpha,\beta).$$

The differential and integral forms are easily shown to be equivalent. The use of fixed nuclei intrinsic states is reflected in the appearance of δ-function kernels. Introducing an uncertainty in the positions of the nuclei spreads out the adiabatic kernels

$$\begin{aligned}\Delta_n(\alpha,\beta)&=\langle\varphi_n(\alpha)\,|\,\varphi_n(\beta)\rangle\,\langle\Phi(\alpha)\,|\,\Phi(\beta)\rangle\,,\\ H_n(\alpha,\beta)&=\langle\varphi_n(\alpha)\,|\,\varphi_n(\beta)\rangle\,\langle\Phi(\alpha)\,|\,T\,|\,\Phi(\beta)\rangle\\ &\quad+\langle\varphi_n(\alpha)\,|\,t\,|\,\varphi_n(\beta)\rangle\,\langle\Phi(\alpha)\,|\,\Phi(\beta)\rangle\\ &\quad+\langle\varphi_n(\alpha)\Phi(\alpha)\,|\,V\,|\,\varphi_n(\beta)\Phi(\beta)\rangle.\end{aligned}\tag{2.13}$$

Since the nuclear intrinsic states are sharply peaked we expect H_n and Δ_n to be essentially different from zero only when $\alpha\cong\beta$.

Solution of either (2.11) or the GHW equation corresponding to (2.12) generates a "band" of levels with corresponding nuclear wf's and weight functions. In view of the limit (2.10) we have

$$\lim_{\Phi\to\delta}E_{nk}^{\mathrm{GCM}}=E_{nk}^{\mathrm{AD}}\,,\quad \lim_{\Phi\to\delta}f_{nk}^{\mathrm{GCM}}=f_{nk}^{\mathrm{AD}}\,,\tag{2.14}$$

where k stands for a set of vibrational and rotational quantum numbers. In replacing $\delta(R-\alpha)$ by $\Phi(R\,|\,\alpha)$ one deforms the adiabatic trial space rather than extending it. Therefore, one can not say anything about the relative magnitude of the GCM and AD eigenvalues. The only conclusion one can draw is that both are upper bounds to the exact energies (both methods are variational). The nonproduct type of wf's, $\Psi_{nk}^{\mathrm{GCM}}(r,R)$, are expected to be of importance in the calculation of properties other than energy, especially for operators involving nuclear coordinates. In the AA, such expectation values are first computed as a function of the internuclear distances. In the GCM, one associates with each property a corresponding kernel which, after a double integration with the weight function, gives the GCM expectation value. For an operator $P=P(r,R)$ we have

$$\begin{aligned}P_n(\alpha,\beta)&=\langle\varphi_n(\alpha)\Phi(\alpha)\,|\,P\,|\,\varphi_n(\beta)\Phi(\beta)\rangle\,,\\ P_{nk}^{\mathrm{GCM}}&=\int\!\!\int f_{nk}(\alpha)P_n(\alpha,\beta)f_{nk}(\beta)\,d\alpha\,d\beta.\end{aligned}\tag{2.15}$$

Nonadiabatic effects are expected to be more pronounced in the calculation of these quantities since adiabatic energies are accurate up to order κ^4 the corresponding wf's only up to κ^2.

III. DIATOMIC MOLECULES

A. Symmetries of the molecular levels

The variational derivation of the adiabatic approximation, common in most textbooks,[22,23] does not yield eigenfunctions of J^2 and J_z, i.e., does not conserve total angular momentum $\vec{J}$. The difficulty stems from the adiabatic correction term $C_n(R)$ being generally not invariant under rotation. It is therefore preferable to take the rotational invariance of H into account from the outset.[21] For this purpose one introduces a rotating reference frame, i.e., a system of axes in which the nuclei are immobile. For diatomics a convenient choice of this molecule-fixed frame (S') relative to the laboratory system (S) is to take the z' axis along the vector $\vec{R}$ joining the nuclei, the y' axis perpendicular to $\vec{e}_z$ and $\vec{e}_{z'}$, and the x' axis such that S' is right-handed when S is. The transformation of an electronic position vector $\vec{r}$ from S to S' is given by[24]

$$\begin{bmatrix}x'\\ y'\\ z'\end{bmatrix}=\begin{bmatrix}\cos\theta\cos\phi & \cos\theta\sin\phi & -\sin\theta\\ -\sin\phi & \cos\phi & 0\\ \sin\theta\cos\phi & \sin\theta\sin\phi & \cos\theta\end{bmatrix}\begin{bmatrix}x\\ y\\ z\end{bmatrix},\tag{3.1}$$

where θ,ϕ are the polar angles of $\vec{R}$ in S. So far we have used electronic states defined in S. However in order to evaluate the adiabatic correction term one has to transform φ_n and T to the rotating frame. It is easily seen that

$$\mathcal{R}(\theta,\phi)\varphi_n(r\,|\,\vec{R})=\varphi_n(r'\,|\,R\vec{e}_{z'})\equiv\varphi_n(r'\,|\,R)\,,\tag{3.2}$$

where φ_n is the electronic state in S' and $\mathcal{R}(\theta,\phi)$ the rotation operator associated with (3.1). Since the electronic coordinates r' depend implicitly upon θ and ϕ, the differentiations with respect to nuclear coordinates will give rise to extra terms if operating on $\varphi_n(r'\,|\,R)$. These additional operators can be divided into two groups. The members of the first group commute with the z' component of the electronic angular momentum $l_{z'}$, while the second group couples states differing in one unit of Λ (common notation for the eigenvalues of $l_{z'}$). If averaged over the electronic eigenstates (which are eigenfunctions of $l_{z'}$) the latter do not contribute. Comparing the remaining term with the expression for the total angular momentum[24]

$$\begin{aligned}J^2=-\Bigg[&\frac{1}{\sin\theta}\,\frac{\partial}{\partial\theta}\,\sin\theta\,\frac{\partial}{\partial\theta}\\ &+\frac{1}{\sin^2\theta}\left(\frac{\partial}{\partial\phi}-il_{z'}\cos\theta\right)^2-l_{z'}^2\Bigg],\end{aligned}\tag{3.3}$$

one finds that T should be replaced by

$$-(1/2\mu)\Delta_R+(1/2\mu R^2)(J^2-l_{z'}^2+l_{x'}^2+l_{y'}^2).\tag{3.4}$$

The adiabatic differential operator [the translational motion is assumed to be separated off] can then be written as

$$-(1/2\mu)\Delta_R + (1/2\mu R^2)(J^2 - \Lambda^2) + W_n(R), \tag{3.5}$$

where J^2_Λ is (3.3) with $l_{z'}$ replaced by Λ. $W_n(R)$ is the sum of the fixed nuclei potential and the pure R dependent terms arising from averaging (3.4) over $\varphi_n(R)$. The eigenfunctions of J^2_Λ are well known.[25] They determine the angular part of the nuclear eigenvalue problem $e^{iM\Phi}d^J_{M\Lambda}(\theta)$. Here $d^J_{M\Lambda}$ is the Wigner function as defined e.g., in Ref. 26. The radial equation for the function $g(R)=Rf(R)$ now takes the form

$$\left(-\frac{1}{2\mu}\frac{d^2}{dR^2}+\frac{J(J+1)-\Lambda^2}{2\mu R^2}+W_n(R)\right)g(R)=Eg(R). \tag{3.6}$$

The electronic eigenstates are traditionally written ${}^{2S+1}\Lambda^{\pm}_{g,u}$. According to whether $\Lambda = 0, 1, 2, \ldots$ one has $\Sigma, \Delta, \Pi, \ldots$ states, ± denotes the behavior under reflection through a plane containing the molecular axis and $2S+1$ stands for the spin multiplicity. We will study the molecular levels built on the above electronic states neglecting all coupling between spin and orbital angular momenta. The final wf's take their most compact form if one defines the azimuthal angles of all electrons relative to the one of a particular electron. If we call this angle ψ one can factorize $e^{i\Lambda\psi}$ from the electronic states and the adiabatic functions are

$$\begin{aligned}&\varphi^{\mathrm{rel}}_\Lambda(r'\,|R)R^{-1}g(R)D^J_{M\Lambda}(\Omega),\\ &D^J_{M\Lambda}(\Omega)=e^{iM\Phi}d^J_{M\Lambda}(\theta)e^{i\Lambda\psi},\end{aligned} \tag{3.7}$$

where $\varphi^{\mathrm{rel}}_\Lambda$ depends on the relative positions of the particles only and Ω denotes the three angles ϕ, θ, ψ. We have not yet taken into account the fact that for $\Lambda \neq 0$ the $\pm\Lambda$ states are degenerate such that the AA could be performed using any linear combination of them. The proper coefficients can. however, easily be found, requiring the final wf's to be of good parity. The result reads

$$\varphi^{\mathrm{rel}}_0(r'\,|R)R^{-1}g(R)Y_{JM}(\theta,\phi)$$

$$[\varphi^{\mathrm{rel}}_\Lambda(r'\,|R)D^J_{M\Lambda}(\Omega)\pm\varphi^{\mathrm{rel}}_{-\Lambda}(r'\,|R)D^J_{M-\Lambda}(\Omega)]R^{-1}g(R), \tag{3.8}$$

for Σ and Δ, Π, . . . states, respectively. Functions defined in S' change sign under inversion of S according to whether they are ± states.[26] In view of this fact and the properties of spherical harmonics and D functions one can summarize the symmetry properties of the molecular levels as follows[26] (see Fig. 1). For $\Sigma^+(\Sigma^-)$ the parity of the rotational levels is $(-)^J\ [(-)^{J+1}]$. In the homonuclear case the electronic states have the additional gerade (g) or ungerade (u) symmetry depending on the behavior under inversion of the electron coordinates alone. The spatial part of total wf must be symmetric (s) or antisymmetric (a) such that after combination with a nuclear-spin function the state changes sign or not under interchange of the nuclei depending on whether the latter are fermions or bosons. There is a definite relationship between the total parity, the sign (±) of the electronic term and the nuclear permutation symmetry. If the level is even (odd) and positive (negative) then it is symmetric, but when it is even (odd) and negative (positive) it is antisymmetric under interchange of the nuclei.

The explicit derivation of the above results is quite tedious and lengthy (explaining why it can be found in specialized books and articles). It is, however, of vital importance to prove that total angular momentum and parity are conserved in the AA. We now aim at showing, in a more unified and didactically appealing way, that the nonadiabatic GCM shares this property. In particular the often confusing transformation of functions and operators to the rotating reference frame will be avoided.

Peierls and Yoccoz[27] were the first to demonstrate that angular-momentum projection can be achieved by the GCM. They observed that the orientation of the reference frame in which the intrinsic state is defined can be used as a generator coordinate. Consider the energetically degenerate functions

$$\mathcal{R}(\Omega)\chi(x)=\chi[\mathcal{R}^{-1}(\Omega)x]\equiv\chi(x\,|\,\Omega). \tag{3.9}$$

One can dispose of the arbitrary directions Ω by integrating over all possible angles, i.e.,

$$\Psi(x)=\int f(\Omega)\chi(x\,|\,\Omega)\,d\Omega). \tag{3.10}$$

The resulting GHW integral equation can be solved by group theoretical methods.[28] The weight functions turn out to be linear combinations of D functions

$$f_{JM}(\Omega)=\sum_{K=-J}^{+J}C_K D^J_{KM}(\Omega)\,, \tag{3.11}$$

where the coefficients C_K are the solutions of the algebraic eigenvalue problem

$$\begin{aligned}&\sum_{K'=-J}^{+J}(H^J_{KK'}-E\Delta^J_{KK'})C_{K'}=0,\\ &H^J_{KK'}=\langle\chi(0)\,|HP^J_{KK'}|\,\chi(0)\rangle\,,\\ &\Delta^J_{KK'}=\langle\chi(0)\,|P^J_{KK'}|\,\chi(0)\rangle.\end{aligned} \tag{3.12}$$

P^J_{MK} is the familiar angular momentum projection operator defined by

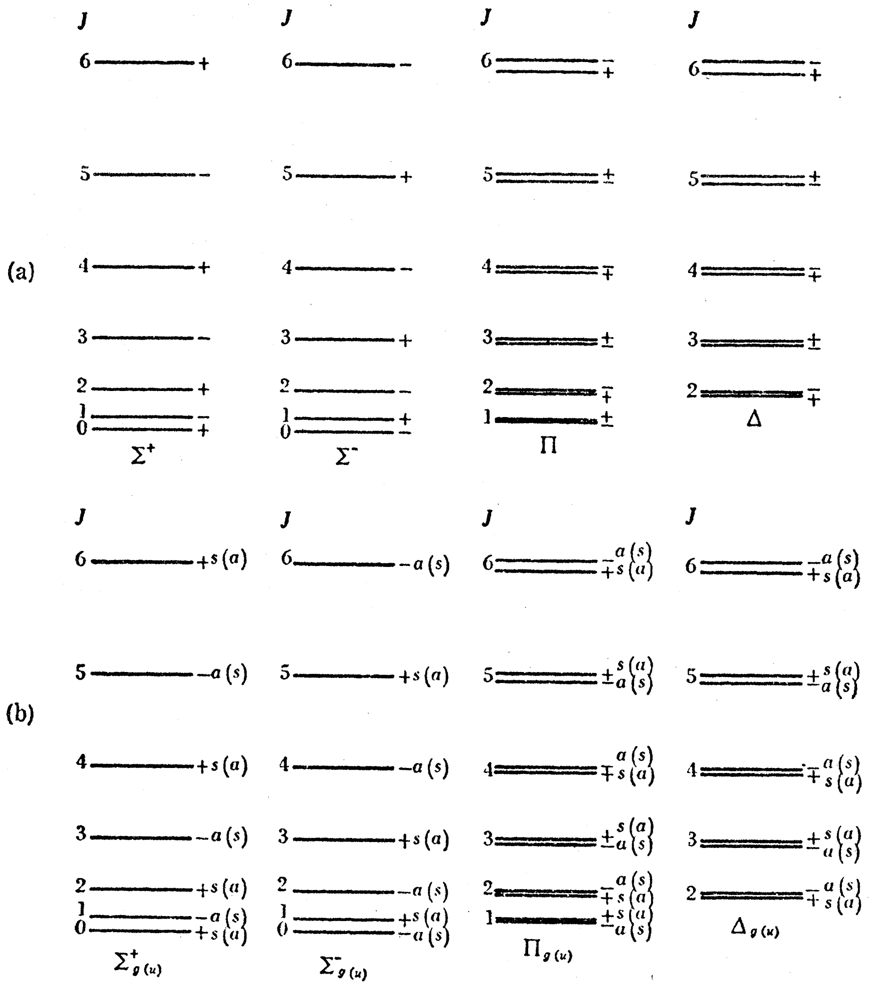

FIG. 1. Symmetry properties of rotational levels in various species of vibrational levels: (a) heteronuclear and (b) homonuclear.

$$P^J_{MK} = \int D^J_{MK}(\Omega)\mathcal{R}(\Omega)\,d\Omega. \tag{3.13}$$

(We left out a constant $(2J+1)/(8\Pi^2)$ since in the following, the equations are frequently valid up to a normalization factor only.) It projects from an arbitrary function an eigenstate of J^2 and J_z with eigenvalues J and M. Combining (3.10), (3.11), and (3.13) the final wf can be written

$$\Psi_J\ (x) = \sum_{K=-J}^{+J} C_K P^J_{MK}\chi(x\,|\,0), \tag{3.14}$$

which is a weighted sum of JM eigenstates.

The above technique is well suited to obtain good angular-momentum quantum numbers in our GCM approach to molecules. In $\Lambda = 0$ and $\Lambda \neq 0$ diatomic electronic states the wf's are

$$\int f(\vec{\alpha})\varphi_0(r\,|\,\vec{\alpha})\Phi(|\vec{R}-\vec{\alpha}|)\,d\vec{\alpha}, \tag{3.15a}$$

$$\int f(\vec{\alpha})[\varphi_\Lambda(r\,|\,\vec{\alpha}) \pm \varphi_{-\Lambda}(r\,|\,\vec{\alpha})]\Phi(|\vec{R}-\vec{\alpha}\,|)\,d\vec{\alpha}. \tag{3.15b}$$

We have restricted the nuclear intrinsic states to depend on $|\vec{R}-\vec{\alpha}|$ because in the adiabatic limit it should go to $\delta(\vec{R}-\vec{\alpha})$ which is an even function of its argument. It is easily seen that with this choice the average relative position of the nuclei in the intrinsic states $\chi(\vec{\alpha})$ is $\vec{\alpha}$, indeed, one finds $\langle\chi(\vec{\alpha})\,|\vec{R}|\,\chi(\vec{\alpha})\rangle = \vec{\alpha}$. A typical choice could be $(\lambda/\pi)^{3/4}\exp[-\lambda(\vec{R}-\vec{\alpha})^2]$. In view of the dependence of the electronic Hamiltonian $H(\vec{\alpha})$ on $|\vec{r}\pm\vec{\alpha}|$ and the form of the nuclear intrinsic states we can rewrite these integrals as

$$\int f(\vec{\alpha})\mathcal{R}(\theta_\alpha, \phi_\alpha)\varphi_0(r\,|\,\alpha\vec{e}_z)\Phi(|\vec{R}-\alpha\vec{e}_z\,|)\,d\vec{\alpha}$$

$$= \int f(\vec{\alpha})\mathcal{R}(\theta_\alpha, \phi_\alpha)\chi_0(\alpha\vec{e}_z)\,d\vec{\alpha},$$

$$\int f(\vec{\alpha})\mathcal{R}(\theta_\alpha, \phi_\alpha)[\varphi_\Lambda(r\,|\,\alpha\vec{e}_z) \pm \varphi_{-\Lambda}(r\,|\,\alpha\vec{e}_z)]$$

$$\times\Phi(|\vec{R}-\alpha\vec{e}_z|)\,d\vec{\alpha}$$

$$= \int f(\vec{\alpha})\mathcal{R}(\theta_\alpha, \phi_\alpha)[\chi_\Lambda(\alpha\vec{e}_z) \pm \chi_{-\Lambda}(\alpha\vec{e}_z)]\,d\vec{\alpha}. \tag{3.16}$$

When $f(\vec{\alpha})$ is split into a radial and angular part one can roughly recognize the form of the projection operators in the above formula. An essential simplification occurs because of the fact that when P^J_{MK} works on an eigenfunction of J_z it will give zero unless the corresponding eigenvalue is K. The basis functions in (3.16) are eigenstates of $J_z = l_z + L_z$ with eigenvalues 0, Λ, and $-\Lambda$. Therefore, one can project out only one JM component for Σ states and two for $\Lambda \neq 0$. In the latter case (3.12) reduces to a 2×2 secular equation. The diagonal elements, i.e., the energies of $P^J_{M\Lambda}\chi_\Lambda$ and $P^J{}_{-\Lambda}\chi_{-\Lambda}$, turnout to be equal. Therefore, the resulting eigenstates are always the ± combinations of the basis functions. Because of these additional features of the molecular intrinsic states, the weight functions are

$$f_{JM}(\vec{\alpha}) = \alpha^{-1} g(\alpha) Y_{JM}(\theta_\alpha, \phi_\alpha),$$

$$f_{JM}(\vec{\alpha}) = \alpha^{-1} g(\alpha)[e^{iM\phi_\alpha} d^J_{M\Lambda}(\theta_\alpha) + e^{iM\phi_\alpha} d^J_{M-\Lambda}(\theta_\alpha)]. \tag{3.17}$$

The associated angular-momentum projected wf's are

$$\Psi_{JM} = \int g(\alpha) P^J_{M0}\chi_0(\alpha\vec{e}_z)\alpha\,d\alpha,$$

$$\Psi_{JM} = \int g(\alpha)[P^J_{M\Lambda}\chi_\Lambda(\alpha\vec{e}_z) \pm P^J_{M-\Lambda}\chi_{-\Lambda}(\alpha\vec{e}_z)]\alpha\,d\alpha. \tag{3.18}$$

The consistency of these results can be tested by verifying that the parity is $(-)^{J+s}$ where s is 0 for a + state and 1 for a − state.

In the homonuclear case, good parity functions can be generated if the electronic g or u states are combined with even or odd nuclear parts

$$\Phi_{G,U}(\vec{R}\,|\,\vec{\alpha}) = \Phi(|\vec{R} - \vec{\alpha}\,|) \pm \Phi(|\vec{R} + \vec{\alpha}\,|). \tag{3.19}$$

The GCM wf's will have parity $(-)^{p+P}$, where p and P are 0 or 1 for gerade or ungerade functions, respectively. Working out the integrals making use of the above projection technique one finds that the terms arising from $\Phi(|\vec{R} \pm \vec{\alpha}\,|)$ are identical up to a sign factor. More specifically the wf's are proportional to

$$[1 + (-)^{J+s+p+P}]. \tag{3.20}$$

This factor determines whether a given electronic state (i.e., a given s and p) and a total angular momentum and parity are compatible. At the same time it tells us which nuclear intrinsic states to use. It is a mere exercise to reconstruct the diagrams of Fig. 1 by requiring (3.20) to be nonvanishing. An interesting situation occurs for spin zero nuclei. In this case there are no antisymmetric spin states such that G basis states are obligatory. It then follows that (3.20) is zero for Σ^+_g, Σ^-_u (Σ^+_u, Σ^-_g) and even (odd) J values. Such levels are therefore nonexisting, a well-known result.[26]

This completes our derivation of the inter-relationship between electronic, nuclear, and final-state quantum numbers which was established via projection techniques rather than by manipulation of rotating reference frames.

B. Λ doubling

In the AA terms with $\Lambda \neq 0$ are doubly degenerate. In reality, however, one finds two levels of opposite parity close together [see e.g., (26)]. This effect is known as Λ doubling. Van Vleck[29] has shown that the AA fails to explain this phenomenon because of the coupling terms dropped in performing the transformation to the rotating reference frame. These operators connect electronic states Λ with $\Lambda \pm 1$. Hence in a PT treatment of Λ doubling, the effect will be of order 2Λ. The energy splitting is therefore estimated to be of the order $(m/M)^{2\Lambda} = \kappa^{\Lambda/2}$, i.e., it is most important for Π terms.

In the GCM approach, Λ doubling is taken into account automatically via the angular momentum projection. Indeed the functions $P^J_{M\Lambda}\chi_\Lambda$ and $P^J_{M-\Lambda}\chi_{-\Lambda}$ are nonorthogonal and interacting with respect to the Hamiltonian. The eigenvalues of the 2×2 secular equation are therefore nondegenerate. The dependence of the level splitting upon the quantum numbers J and Λ can be calculated using techniques to be presented in Sec. III C. One finds

$$\Delta E_{J\Lambda} = \text{const}\binom{J+\Lambda}{J-\Lambda}, \tag{3.21}$$

where the parentheses denote a binomial coefficient. This result (I am not aware of any previous derivation of (3.21).) is identical to the one obtained by PT following the AA [$J(J+1)$ for Π states, $(J-1)J(J+1)(J+2)$ for Δ states, etc.]

Λ doubling, although small, is experimentally observed. It is a nonadiabatic effect which is incorporated in the GCM picture due to the interaction between the JM projections of χ_Λ and $\chi_{-\Lambda}$.

C. Separation of the molecular energies

One of the great successes of the AA is that the energy pattern

$$E \cong E_{\text{trans}} + E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}}, \tag{3.22}$$

which roughly explains the structure of the spectra, can be obtained in a simple way. Expanding the potential $W_n(R)$ around its minimum R_0 one obtains, to second order, a harmonic oscillator equation yielding the approximate spectrum

$$E_{nvJ} = W_n(R_0) + (v + \tfrac{1}{2})\omega + [J(J+1) - \Lambda^2]/2I,$$
$$\omega = [W''(R_0)/\mu]^{1/2}, \quad I = \mu R_0^2, \tag{3.23}$$

where $v = 0, 1, 2, \ldots$ and J takes on integral values equal or superior to Λ.

The decomposition (3.22) results from the assumption that the electronic, rotational, and nuclear vibrational motions are decoupled. This is reflected in the product type of the corresponding wave function. The question now arises whether it is possible to approximately solve the GCM equation such that the energy can be written as in (3.22) without having to actually separate the dynamical motions. For this purpose, we evaluate the energy of the GCM projected states. As an example we treat Σ states. The results are easily generalized to the $\Lambda \neq 0$ case. We have

$$E_{nJ} = \int\int g(\alpha) \langle \chi_0(\alpha) | (P_{\mathrm{MO}}^J)^+ H P_{\mathrm{MO}}^J | \chi_0(\beta) \rangle g(\beta) \alpha\beta \, d\alpha \, d\beta$$
$$\times \left(\int\int g(\alpha) \langle \chi_0(\alpha) | (P_{\mathrm{MO}}^J)^+ \; P_{\mathrm{MO}}^J | \chi_0(\beta) \rangle g(\beta) \alpha\beta \, d\beta \, d\beta \right)^{-1}. \tag{3.24}$$

Using the properties of the projection operators, we can rewrite this as

$$E_{nJ} = \int\int g(\alpha) \left[\int \langle \chi_0(\alpha) | H \mathcal{R}(\theta_\beta) | \chi_0(\beta) \rangle P_J(\theta_\beta) \, d\theta_\beta \right] g(\beta) \alpha\beta \, d\alpha \, d\beta$$
$$\times \left(\int\int g(\alpha) \left[\int \langle \chi_0(\alpha) | \mathcal{R}(\theta_\beta) | \chi_0(\beta) \rangle P_J(\theta_\beta) \, d\theta_\beta \right] g(\beta) \alpha\beta \, d\alpha \, d\beta \right)^{-1}, \tag{3.25}$$

where the $P_J(\theta_\beta)$ are the Legendre polynomials (we will drop the β subscript for the rotation angle). In view of the fact that the nuclear basis states are strongly localized in space, the matrix elements occurring in the above integrals are sharply peaked functions of $\alpha - \beta$ and will decrease rapidly as θ differs from 0 or π. It is therefore reasonable, in a first approximation, to replace the overlap matrix element in the denominator of (3.25) by a product of two Gaussians

$$e^{-(r/2)\theta^2} e^{-(s/2)(\alpha-\beta)^2} = \Delta_{\mathrm{rot}}(\theta) \Delta_{\mathrm{vib}}(\alpha - \beta). \tag{3.26}$$

The Hamiltonian matrix element will behave in approximately the same way, so that the ratio $K(\alpha, \beta, \theta)$ is a slowly varying function. We therefore set

$$K(\alpha, \beta, \theta) \cong E(\alpha_0) + K_{\mathrm{vib}}(\alpha, \beta) + K_{\mathrm{rot}}(\theta)$$
$$= E(\alpha_0) + \tfrac{1}{2} s [B(\alpha - \alpha_0)^2 + 2A(\alpha - \alpha_0)$$
$$\times (\beta - \alpha_0) + B(\beta - \alpha_0)^2] - \tfrac{1}{2} r C \theta^2, \tag{3.27}$$

where $\cong$ means α and β are around α_0 and θ is in the neighborhood of 0 or π.

The constants $s, r, A, \ldots$ are easily determined by expanding the intrinsic states in Taylor series around $\theta = 0$ and $\alpha = \beta = \alpha_0$. One obtains

$$s = \left\langle \frac{\partial \chi_0}{\partial \alpha} \middle| \frac{\partial \chi_0}{\partial \alpha} \right\rangle_0, \quad r = \langle \chi_0 | J_y^2 | \chi_0 \rangle_0,$$
$$sB = \langle \chi_0 | H - E(\alpha_0) \left| \frac{\partial^2 \chi_0}{\partial \alpha^2} \right\rangle_0, \tag{3.28}$$

$$sA = \left\langle \frac{\partial \chi_0}{\partial \alpha} \middle| H - E(\alpha_0) \middle| \frac{\partial \chi_0}{\partial \alpha} \right\rangle_0,$$
$$rC = \langle \chi_0 | H J_y^2 - E(\alpha_0) | \chi_0 \rangle_0,$$

where $\langle \; \rangle_0$ means that the matrix elements have to be taken at $\theta = 0$, $\alpha = \beta = \alpha_0$. The energy expectation value is then a sum of three terms

$$E_{nJ} = E(\alpha_0) + \int P_J(\theta) K_{\mathrm{rot}}(\theta) \Delta_{\mathrm{rot}}(\theta) \, d\theta$$
$$\times \left(\int P_J(\theta) \Delta_{\mathrm{rot}}(\theta) \, d\theta \right)^{-1}$$
$$+ \int\int g(\alpha) K_{\mathrm{vib}}(\alpha, \beta) \Delta_{\mathrm{vib}}(\alpha - \beta) g(\beta) \alpha\beta \, d\alpha \, d\beta$$
$$\times \left(\int\int g(\alpha) \Delta_{\mathrm{vib}}(\alpha - \beta) g(\beta) \alpha\beta \, d\alpha \, d\beta \right)^{-1}. \tag{3.29}$$

Since the integrands in θ have nonzero values only around 0 and π, one can insert the asymptotic expansion of the Legendre polynomials

$$P_J(\theta) \underset{\theta \to 0}{\sim} 1 - \tfrac{1}{4} \theta^2 J(J+1). \tag{3.30}$$

This allows us to evaluate the second term in (3.29) in closed form. The function $g(\alpha)$ has so far been left arbitrary. If it is varied to minimize the last term in (3.29) one obtains a harmonic oscillator equation for the function $\int \Delta_{\mathrm{vib}}(\alpha - \beta) g(\beta) \beta \, d\beta$. The approximations made so far are commonly known as the Gaussian overlap approximation (3.26) and the quadratic approximation (3.27) and (3.30). The resulting energy spectrum under these conditions is

$$\begin{aligned} E_{nvJ} &= E(\alpha_0) - \Delta E_{\text{vib}} - \Delta E_{\text{rot}} \\ &\quad + (v+\tfrac{1}{2})\omega + J(J+1)/2I, \\ \Delta E_{\text{vib}} &= \tfrac{1}{2}A, \quad \omega = (A^2 - B^2)^{1/2}, \\ \Delta E_{\text{rot}} &= C, \quad I = r/C, \end{aligned} \tag{3.31}$$

which is the required form. The term ΔE_{vib}, ΔE_{rot} represent the energy gain due to the variational treatment of vibrations and rotations. The vibration frequency ω and the moment of inertia I depend upon the local structure of the energy surface around the equilibria $\alpha = \alpha_0$ and $\theta = 0, \pi$. For the $\Lambda \neq 0$ case one has to use the expansion

$$d^J_{\Lambda\Lambda}(\theta) \underset{\theta \to 0}{\sim} 1 - \tfrac{1}{4}\theta^2[J(J+1) - \Lambda^2], \tag{3.32}$$

which gives (2.23). For a detailed calculation of the moments of inertia we refer to the nuclear physics literature.[30]

The energy formula (3.31) has here been derived as a result of mathematical approximations rather than through decoupling dynamical motions. It is important to notice that although the weight functions factorize as a product of a rotational and vibrational part the corresponding wave functions do not. The harmonic GCM approximation (Gaussian overlap plus quadratic approximation) is therefore a nonadiabatic zeroth-order problem.

IV. CONCLUSION

We have shown that it is possible to formulate a theory of molecular spectra without using potential energy surfaces. The GCM shares the simplifying features of the adiabatic approximation: it makes use of work on electronic problems (electronic part of intrinsic states), total parity and angular momentum are conserved and the separation of the eigenenergies is obtained through mathematical approximations. It will be hard to convince both theoreticians and experimentalists to abandon the potential-energy curve picture, a concept which has served a useful purpose for over fifty years. We aim to show that nonadiabaticity is indeed an important effect in the calculation of molecular properties and that the GCM is a feasible method to incorporate them. Work along these lines and generalization of Sec. III to the polyatomic case is in progress.

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