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When and Why Hund's Cases Arise

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The conditions are found under which the general diatomic molecule equation reduces to the set of equations for certain Hund's cases. The relations between some operators are given which are basic in characterizing a molecule as belonging to a definite Hund's case on the basis of approximate nonempirical calculations. The accurate quantum mechanical explanation is given for a transition between Hund's cases when such a physical quantity as the rotational or vibrational quantum number varies.

1. INTRODUCTION

To describe rotational–vibrational electronic spectra, Hund has introduced definite momentum coupling cases for diatomic molecules which are now well known and widely used (*1–3*). Presently, the treatment can be carried out for a great variety of electronic states both for ideal and intermediate Hund's cases (*3*). All such treatments are based on the proper model Hamiltonian for each Hund's case. At the same time, there is still no strict theory which could on the basis of some nonempirical calculations characterize a molecule as belonging to one of the ideal or intermediate cases. But modern calculation capabilities give good reason to hope that this problem for the diatomic molecules could be solved if the needed theory existed.

It is doubtless that as a basis for the treatment of the rotational–vibrational electronic spectra, use should be made of the equation which is invariant under rotation of the system as a whole and translation of its center of mass. A convenient form of such equation was proposed by Pack and Hirschfelder (*4*), who constructed later, using this equation, the best adiabatic approximation (*5*). In this paper, various Hund's cases are discussed on the basis of the exact electronic nuclear set of equations. Though Pack and Hirschfelder (*5*) briefly examined the equations for Hund's cases "a" and "c", they did not give reason for other Hund's cases to arise. We have obtained here definite conditions on the operators from the total equation, under which the molecular system would be brought closer to one of Hund's cases. This treatment also enables us to clarify and describe the observed change of Hund's cases as the rotational or vibrational quantum number varies.

2. GENERAL EQUATION FOR DIATOMIC MOLECULES

Let us consider a diatomic molecule Schrödinger equation which in the absence of any external field is invariant under the center-of-mass translation and rotation of the system as a whole. The total Hamiltonian is given by

$$H_t = \sum_\alpha \frac{1}{2m_\alpha} P_\alpha^2 + \sum_i \tfrac{1}{2} P_i^2 + \sum_{i<j} V_{ij} + \sum_{i,\alpha} V_{i\alpha} + \sum_{\alpha<\beta} V_{\alpha\beta} + \alpha^2 H_\alpha, \tag{1}$$

where P_α, P_i are the momentum of nuclei and electrons, V_{ij}, $V_{i\alpha}$, $V_{\alpha\beta}$ are the potential energies of two electrons, of an electron and a nucleus and of two nuclei, respectively, and $\alpha^2 H_a$ contains the relativistic and magnetic corrections accurate through $O(\alpha^2)$ where α is the fine-structure constant *(6)*. To separate the center-of-mass motion and rotation we proceed to the coordinate system related to the center of mass of the nuclei and to the body-fixed coordinate system. The so obtained Hamiltonian which governs the internal motion of the system is given by *(4)*

$$\mathbf{H} = \frac{1}{2\mu} P_R^2 + \frac{\mathbf{L}_R^2}{2\mu R^2} + H_e + \frac{1}{\mu} H_\mu + \alpha^2 H_\alpha, \tag{2}$$

where $\mathbf{L}_R$ is the relative orbital angular momentum of the two nuclei, H_e is the sum of the kinetic and potential energy for the N electrons, and $1/\mu H_\mu$ is a mass polarization correction. We now represent $\mathbf{L}_R$ by

$$\mathbf{L}_R = \mathbf{J} - \mathbf{J}_e,$$

where $\mathbf{J}$ is a total angular momentum of the system and $\mathbf{J}_e$ is a total electronic angular momentum. This completes the transformation of the Hamiltonian in representation of the eigenfunctions of $\mathbf{J}^2$ and $\mathbf{J}_z$. Since the dimension of the rotation group representation is more than (or equal to) one the resulting equation has a matrix form (except $J = 0$)

$$\mathbf{H}\Psi(r, R; J, \Omega) = E\Psi(r, R; J, \Omega), \tag{4}$$

$$H_{\Omega\Omega-1}\Psi(\mathrm{J}, \Omega - 1) + H_{\Omega\Omega}\Psi(J, \Omega) + H_{\Omega\Omega+1}\Psi(J, \Omega + 1) = E\Psi(J, \Omega), \tag{5}$$

$$H_{\Omega\Omega} = \frac{1}{2\mu} P_R^2 + \frac{1}{2\mu R^2}[J(J+1) - 2\Omega^2 + \mathbf{J}_e^2] + H_e + \frac{1}{\mu} H_\mu + \alpha^2 H_\alpha, \tag{6}$$

$$H_{\Omega\Omega\pm1} = -\frac{\lambda_\pm(J, \Omega)}{2\mu R^2} \mathbf{J}_{e\mp}, \tag{7}$$

$$\lambda_\pm(J, \Omega) = [(J \pm \Omega + 1)(J \mp \Omega)]^{\frac{1}{2}}. \tag{8}$$

Equation (4) yields different sets of energy levels for different J's. We simplify the problem by the electronic nuclear separation. First we represent the internal wavefunction in an exact form

$$\Psi = \Phi(r,R) \cdot \chi(R), \tag{9}$$

where Ψ is a column vector, Φ is a column vector of electronic functions and $\chi(R)$ is a nuclear function.

$$\langle \Phi | \Phi \rangle_r = 1, \tag{10}$$

$$\langle \chi | \chi \rangle_R = 1. \tag{11}$$

By applying a variational principle with a trial function in the form of Eq. (9) and normalization conditions Eqs. (10, 11) we obtain a matrix electronic equation (12) and one-dimensional nuclear equation (15) instead of Eq. (4).

$$H_{\Omega\Omega-1}{}^{e}\Phi(J,\Omega-1)+H_{\Omega\Omega}{}^{e}\Phi(J,\Omega)+H_{\Omega\Omega+1}{}^{e}\Phi(J,\Omega+1)=E_e(R)\Phi(J,\Omega), \quad (12)$$

$$H_{\Omega\Omega}{}^{e}=H_e+\frac{1}{\mu}H_\mu+\alpha^2H_\alpha+\frac{1}{2\mu R^2}(\mathbf{J}_{ex}{}^2+\mathbf{J}_{ey}{}^2-\Omega^2)+\frac{1}{2\mu}P_R{}^2-\frac{1}{\mu}\left(\frac{\nabla_R\chi}{\chi}\right)\nabla_R, \quad (13)$$

$$H_{\Omega\Omega\pm1}{}^{e}=-\frac{\lambda_\pm(J,\Omega)}{2\mu R^2}\mathbf{J}_{e\mp}, \quad (14)$$

$$\left\{\frac{1}{2\mu}P_R{}^2+E_e(R)+\frac{1}{2\mu R^2}J(J+1)\right\}\chi(R)=E\chi(R). \quad (15)$$

Equation (12) can be reduced to the best adiabatic equations (5) by neglecting the term

$$(1/\mu)(\nabla_R\chi/\chi)\nabla_R, \quad (16)$$

in the electronic equation. Thereafter the familiar picture of energy levels is obtained, i.e., a number of vibrational states belongs to one electronic state.

The neglect of only one term (16) in the set of equations (12)–(15) is not very useful since it does not result in obtaining an equation for which solutions are known, or at least, for which an analytical method of solution is available. So we take as a nonperturbed initial equation the simplest diagonal electronic equation

$$H_e\Phi(J,\Omega)=E_e(R)\Phi(J,\Omega), \quad (17)$$

which is moreover J-independent. The rest of the terms in the electronic equation will be considered as perturbations

$$-\frac{\lambda_\pm}{2\mu R^2}\mathbf{J}_{e\mp}, \quad (18)$$

$$\alpha^2H_\alpha \quad (19)$$

$$\frac{1}{2\mu}P_R{}^2, \quad (20)$$

$$-\frac{1}{\mu}\left(\frac{\nabla_R\chi}{\chi}\right)\nabla_R, \quad (21)$$

$$\frac{1}{2\mu R^2}(\mathbf{J}_{ex}{}^2+\mathbf{J}_{ey}{}^2-\mathbf{J}_{ez}{}^2), \quad (22)$$

$$\frac{1}{\mu}H_\mu. \quad (23)$$

It is clear that depending upon the problem different perturbations are essential. Some of them may be large enough to be included in the zero order Hamiltonian. In particular, we shall be interested in interrelations between the operators (18–23) at various Hund's cases or vice versa under what conditions on the perturbations (18)–(23) one or another Hund's case arises.

Now we outline the operators (18)–(23).

(18) is the operator responsible for the electron orbital-rotational and spin-rotational couplings (Coriolis interactions).

(19) is the relativistic term from the Breit–Pauli expansion accurate through $O(\alpha^2)$.

(20) This term in an electronic equation is not taken to mean the nuclear kinetic energy. It takes into account nonsynchronism of electronic nuclear motions, i.e., the nonlocality of the electronic equation with respect to variable (parameter) R.

(21) This term also makes a nonlocal contribution to the electronic equation but moreover it modifies the electronic potential valid for a number of vibrational states so that it fits best one of the vibrational states. If the nonadiabaticy is believed to arise when one potential function cannot be valid for more than one vibrational state, the operator (21) may be considered as a nonadiabatic part of the initial Hamiltonian.

The operators (20), (21) lead to disappearance of the symmetry group $O(2)$, i.e., the rotation around the internuclear axis. The initial problem has the rotation group around the center of mass of the system as its symmetry group. This group certainly contains an infinite number of subgroups $O(2)$ with the rotation axis running through the center of mass. But it is easy to see that the center of mass of the whole system does not lie on the internuclear axis. So the symmetry group $O(2)$ for the fixed-nuclei electronic equation gets broken when the nuclear motion is taken into account.

(22) is a term responsible for the fact that the electronic function is not an eigenfunction of $\mathbf{J}_e^2$.

(23) is a mass polarization correction.

3. EQUATIONS FOR DIFFERENT HUND'S CASES

We consider the change of the equations if additional "good" quantum numbers are introduced. This corresponds to the choice of a certain Hund's case. Case "a" corresponds to the introduction of Λ, a projection of the orbital angular momentum on the internuclear axis; Σ, a projection of the spin angular momentum on the internuclear axis; and S, total spin. Introduction of K, an eigenvalue of an operator $\mathbf{K}^2 = (\mathbf{J} - \mathbf{S})^2$, Λ, and S corresponds to Hund's case "b". Case "c" corresponds to the general formulation of the problem without any simplifications. The eigenvalue of $\mathbf{L}_R{}^2$ being a "good" quantum number characterizes both cases "d" and "e". For the case "d" S and an eigenvalue K of an operator $\mathbf{K}^2 = (\mathbf{L}_R + \mathbf{L}_e)^2$ are introduced, which is not, so far, case "e". We shall not be interested in the differences between cases "d" and "e", so we shall combine them and treat them simultaneously as a "good" L_R case.

We now write down the equations resulting from Eq. (12) after introducing additional quantum numbers. No perturbation is neglected for a while. Keeping in mind that a "good" quantum number is an approximate one, the raising and lowering operators for such a "good" quantum number should be kept in the Hamiltonian. Under these assumptions we have the Hamiltonian for the case "a".

$$H_{\Omega\Omega}{}^{a} = H_e + \frac{1}{\mu}H_\mu + \alpha^2 H_\alpha + \frac{1}{2\mu}P_R{}^2 - \frac{1}{\mu}\left(\frac{\nabla_R \chi}{\chi}\right)\nabla_R + \frac{1}{2\mu R^2} \times [\mathbf{L}_{ex}{}^2 + \mathbf{L}_{ey}{}^2 + \mathbf{S}_+\mathbf{L}_{e-} + \mathbf{S}_-\mathbf{L}_{e+} - \Omega^2 - \Sigma^2], \tag{24}$$

$$H_{\Omega\Omega\pm1}{}^{a} = -\frac{\lambda_\pm(J,\Omega)}{2\mu R^2}\mathbf{J}_{e\mp}, \tag{25}$$

$$H_n{}^{a} = \frac{1}{2\mu}P_R{}^2 + \frac{1}{2\mu R^2}[J(J+1) + S(S+1)] + E_e(R). \tag{26}$$

For the case "b" we introduce a new angular momentum

$$\mathbf{K} = \mathbf{L}_R + \mathbf{L}_e, \tag{27}$$

and use the expression

$$\mathbf{L}_R{}^2 = K(K+1) + \Lambda^2 + \mathbf{L}_{ex}{}^2 + \mathbf{L}_{ey}{}^2 - (\mathbf{J}_+\mathbf{L}_{e-} + \mathbf{J}_-\mathbf{L}_{e+}) + (\mathbf{S}_+\mathbf{L}_{e-} + \mathbf{S}_-\mathbf{L}_{e+}). \tag{28}$$

This leads to the following Hamiltonian for Hund's case "b".

$$H_{\Omega\Omega}{}^{b} = H_e + \frac{1}{\mu}H_\mu + \alpha^2 H_\alpha + \frac{1}{2\mu}P_R{}^2 - \frac{1}{\mu}\left(\frac{\nabla_R \chi}{\chi}\right)\nabla_R + \frac{1}{2\mu R^2} \times [\mathbf{L}_{ex}{}^2 + \mathbf{L}_{ey}{}^2 + \mathbf{S}_+\mathbf{L}_{e-} + \mathbf{S}_-\mathbf{L}_{e+} - \Lambda^2], \tag{29}$$

$$H_{\Omega\Omega\pm1}{}^{b} = -\frac{1}{2\mu R^2}\lambda_\pm(J,\Omega)\mathbf{L}_{e\mp}, \tag{30}$$

$$H_n{}^{b} = \frac{1}{2\mu}P_R{}^2 + \frac{1}{2\mu R^2}K(K+1) + E_e(R). \tag{31}$$

The set of equations for the case "c" is completely analogous to Eqs. (12)–(15) and there is no great point in rewriting them.

For cases "d" and "e" the equations are identical

$$H_{\Omega\Omega}{}^{de} = H_e + \frac{1}{\mu}H_\mu + \alpha^2 H_\alpha + \frac{1}{2\mu}P_R{}^2 - \frac{1}{\mu}\left(\frac{\nabla_R \chi}{\chi}\right)\nabla_R, \tag{32}$$

$$H_{\Omega\Omega\pm1}{}^{de} = 0, \tag{33}$$

$$H_n{}^{de} = \frac{1}{2\mu}P_R{}^2 + \frac{L_R(L_R+1)}{2\mu R^2} + E_e(R). \tag{34}$$

The eigenvalue L_R is strictly conserved here because there are no laddering operators in (32)–(34). Such a form is rather simple and convenient for further use.

4. OPERATOR CONDITIONS FOR HUND'S CASES

Having written the equations for all Hund's cases we can answer the question: What conditions have to be fulfilled to reduce the general equations (12)–(15) to particular ones. We shall seek the answer in the form of perturbation operator relations.

We begin with the "good" L_R case, i.e., "d" or "e". It is necessary to account for conditions reducing the general set (12)–(15) to (32)–(34). Comparing these sets of equations shows that two equalities have to be satisfied for this limiting case.

$$\langle\Phi\,|\,\mathbf{J}_e^2 - 2\mathbf{J}_{ez}^2\,|\,\Phi\rangle_r \sim 0, \tag{35}$$

$$\langle\Phi\,|\,\mathbf{J}_{e\pm}\,|\,\Phi\rangle_r \sim 0. \tag{36}$$

Conditions (35), (36) are fulfilled if the solution Φ is an eigenfunction of $\mathbf{J}_e^2$ with a zero eigenvalue. When Φ is an eigenfunction of $\mathbf{J}_e^2$ with a nonzero eigenvalue and also an eigenfunction of $\mathbf{J}_{ez}$, Eq. (35) may be satisfied albeit occasionally for some values J_e and J_{ez} which are integer solutions of an equation

$$J_e(J_e + 1) - 2J_{ez}^2 = 0. \tag{37}$$

(half-integer ones can not be obtained here). The solutions of Eq. (37) are $J_e = 0$, $J_{ez} = 0$; $J_e = 1$, $J_{ez} = \pm 1$; $J_e = 8$, $J_{ez} = \pm 6$, etc. If a function is not an eigenfunction of $\mathbf{J}_e^2$, equality (35) may not be fulfilled. For example, (35) is fulfilled for $J_{ez} = 0$ only if $J_e = 0$. Consequently, a function Φ must not be an eigenfunction of $\mathbf{J}_e^2$ and $\mathbf{J}_{ez}$ (except $J_e = 0$) for Eq. (35)–(36) to be satisfied. Hence, the eigenfunctions of $\mathbf{J}_{ez}$ are not typical for the case under consideration and this physically agrees with accepted angular momentum coupling in Hund's cases "d" and "e". The nonperturbed equation (17) leads to eigenfunctions of $\mathbf{J}_{ez}$. Hence to obtain an accurate description of cases "d" and "e" one must not omit perturbations which break down the $O(2)$ symmetry with respect to an axis running through the nuclei (i.e., lead to functions which are not eigenfunctions of $\mathbf{J}_{ez}$). Such perturbations are operators (20), (21).

The outlined way leads to the conditions on the perturbation operators for Hund's cases "d" and "e".

(1de) The most important perturbation is

$$-\frac{1}{2\mu}\Delta_R - \frac{1}{\mu}\left(\frac{\nabla_R \chi}{\chi}\right)\nabla_R,$$

(2de) The expectation value of the operators (18), (22) over the solutions are close to zero[1] (conditions (35), (36)).

Cases "d" and "e" may be distinguished by the contribution given by the perturbation $\alpha^2 H_\alpha$. Transition to case "e" takes place as this contribution increases.

We represent here the criterion for occurrence of the cases "d", "e" when solutions Φ of a zero-order equation (17) are known.

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[1] Estimates for operators are given here from first-order perturbation theory. Since the corrections have to be small, perturbation theory is valid and its first-order yields a reasonable answer.

(3de) Cases "d" and "e" occur if one of the following relations is satisfied.

$$\langle\Phi|\,\mathbf{J}_e{}^2|\Phi\rangle_r \sim 0, \tag{38}$$

$$\left|\langle\Phi|\frac{1}{2\mu}\Delta_R|\Phi\rangle_r + \cdots\right| > \left|\langle\Phi|\frac{1}{2\mu R^2}[\mathbf{J}_{ex}{}^2 + \mathbf{J}_{ey}{}^2 - \mathbf{J}_{ez}{}^2]|\Phi\rangle_r + \cdots\right|, \tag{39}$$

where $+\cdots$ denotes the higher-order corrections of the perturbation theory for operators (20), (21) on the left side and for (22) on the right side of the inequality.

Let's proceed now to the case "a". The corresponding conditions for its realization are evident enough. A solution must have definite Λ and Σ; thus, the relativistic term should be negligible. In addition operators (18) and

$$\mathbf{S}_{-}\mathbf{L}_{e+} + \mathbf{S}_{-}\mathbf{L}_{e+} \tag{40}$$

must weakly affect the solution. (Ideally both operators (18) and (40) are equal to zero but some neighborhood of the limiting case is of great interest.) Without any great difficulty one obtains the proper conditions on the operators for Hund's case "a".

(1a) It is necessary for the expectation value of the following operators over the solutions to be small.

$$\langle\Phi|\alpha^2 H_\alpha|\Phi\rangle_r \sim 0, \tag{41}$$

$$\langle\Phi|\frac{1}{2\mu R^2}\mathbf{J}_{e\pm}|\Phi\rangle_r \sim 0, \tag{42}$$

$$\langle\Phi|\,\mathbf{S}_{+}\mathbf{L}_{e-} + \mathbf{S}_{-}\mathbf{L}_{e+}|\Phi\rangle_r \sim 0. \tag{43}$$

The condition becomes sufficient if it is supplemented with additional ones.

(2a) The expectation value of an operator (20) is small

$$\langle\Phi|\frac{1}{2\mu}P_R{}^2|\Phi\rangle_r \sim 0. \tag{44}$$

(3a) The Operator $\mathbf{S}_x{}^2 + \mathbf{S}_y{}^2$ has various matrix elements

$$\langle\Sigma,\Lambda,S,n|\,\mathbf{S}_x{}^2 + \mathbf{S}_y{}^2|\Sigma',\Lambda',S',n'\rangle_r = \delta_{nn'}\delta_{SS'}\delta_{\Lambda\Lambda'}\delta_{\Sigma\Sigma'}[S(S+1) - \Sigma^2]. \tag{45}$$

Consider next the case "b". A comparison of Eqs. (12)–(15) with Eqs. (29)–(31) shows that the diagonal operator $\mathbf{S}_x{}^2 + \mathbf{S}_y{}^2$ as well as the nondiagonal $\mathbf{S}_\pm$ disappear when transition to case "b" occurs. This enables us to write down the operator relations for the case "b".

(1b) The relativistic corrections are small:

$$\langle\Phi|\alpha^2 H_\alpha|\Phi\rangle_r \sim 0. \tag{46}$$

(2b) Matrix elements of $\mathbf{L}_{e\pm}$ and $\mathbf{S}_\pm$ differ in order of magnitude and

$$\langle\Phi|\,\mathbf{L}_{e\pm}|\Phi\rangle_r \gg \langle\Phi|\,\mathbf{S}_\pm|\Phi\rangle_r \sim 0. \tag{47}$$

(3b) Inequality (48) is satisfied for the matrix elements of (22) (by its parts to be more precise).

$$\langle \Phi | \mathbf{S}_+\mathbf{L}_{e-} + \mathbf{S}_-\mathbf{L}_{e+} | \Phi \rangle_r > \langle \Phi | \mathbf{S}_+\mathbf{S}_- - \mathbf{S}_z^2 - (2\mathbf{L}_z + 1)\mathbf{S}_z | \Phi \rangle_r. \qquad (48)$$

(4b) The operator $\mathbf{L}_{e\pm}$ itself gives a small contribution

$$\langle \Phi | \mathbf{L}_{e\pm} | \Phi \rangle_r \sim \text{small}. \qquad (49)$$

Criteria for the existence of cases "d" and "b" are obtained from a known solution of Eq. (17) directly by substituting the approximate function for the exact one in Eqs. (41)–(43) and (46)–(49).

The conditions for Hund's case "c" to arise are clear.

(1c) The relativistic corrections are large.

(2c) The expectation value of operators (18)–(20) are small.

Thus all the conditions corresponding to the various Hund's cases are summarized. One should mention that only the operator (23) was not included in any condition, i.e., it does not affect Hund's cases; the others are essential.

5. HUND'S CASES VIA PHYSICAL QUANTITIES

5.1. Rotational Quantum Number Dependence

Consider the inequality (47) as the rotational quantum number J varies, from the point of view of a transition from Hund's case "a" to "b". The right-hand side of inequality (47) is J-independent because S is a "good" quantum number. At the same time the left-hand side of the inequality may be J-dependent. If the nuclear motion is not completely responsible for the total angular momentum $\mathbf{J}$ (that would be a "good" L_R case which is not under consideration now), then an increase of J results in some effective increase of L_e, although L_e may not be well defined. Hence, as J becomes greater the left-hand side of Eq. (47) does the same and so the inequality may become valid as J increases. The same reasoning is valid for inequality (48). This means that as J increases case "a" tends to turn into case "b".

Another tendency in the dependence of Hund's cases on rotational quantum number may be explained qualitatively if one takes into account that the increase of J may be considered as a transition to the region where quasiclassical theory is valid (*7*). Then use may be made of the results obtained by Maslov concerning quasiclassical asymptotics (*8*) for nonlinear equations produced by variational principles. These results show a significant increase of the nonlinear term contribution to the asymptotic region. Although the accurate asymptotic formula is not valid for such nonlinearity as in Eqs. (13)–(15) the qualitative result remains valid: an increase of J may be accompanied by a transition to case "d" or "e". Since the nonadiabatic corrections decrease rapidly down as the reduced mass increases such a transition can take place apparently for light molecules only. If that is so, a transition to the case "d" comes into being because the relativistic terms for light molecules are negligible. This does explain the experimentally observed transition from Hund's case "b" to "d" as J increases for H_2, He_2 molecules (*1*).

5.2. *Vibrational Quantum Number Dependence*

Consider now the vibrational quantum number dependence of Hund's cases. So far an electronic equation has been under consideration (though a nuclear equation has also been written down). On the other hand a quantum number dependence may only be obtained from the nuclear equation. Indeed the electronic equation solution depends parametrically on R, i.e., there is a solution for each point R. So one can say that the above mentioned inequality is fulfilled only for some fixed R values. It is evident that different Hund's cases can take place for different R's. For example, a transition from "e" to "c" would occur, as R increases, because the contribution of Δ_R goes to zero while the relativistic corrections remain finite (*1*, *9*). There is a good reason to suggest that case "c" becomes free of a case "b" admixture as R increases since all the quantities in a proper inequality for the case "b" become very small. In the region where R is small ($R \ll R_e$) the contribution connected with ∇_R and Δ_R seems to become larger quite rapidly, so the cases "d" and "e" predominate at R close to zero.

Thus the potential curve from the electronic equation is divided into several regions corresponding to the various Hund's cases. If one singles out from the electronic energy E(R) the part $E_0(R)$ that is independent of any particular Hund's case, then the residual $E^h(R)$ will be responsible for causing the observed Hund's case to arise. Thus one may consider $E_0(R)$ to be a solution of Eq. (17) and $E^h(R)$ be connected with perturbations (18)–(23). The nuclear equation may be written as

$$\left\{\frac{1}{2\mu}P_R^2 + \frac{J(J+1)}{2\mu R^2} + E_0(R) + E^h(R)\right\}\chi = E\chi. \tag{50}$$

We suppose $E^h(R)$ to be small and apply perturbation theory through the first-order. The corresponding correction

$$\langle\chi|E^h(R)|\chi\rangle \tag{51}$$

may be connected with only one kind of Hund's case corrections if and only if a function χ is localized in that region of R where the potential curve is described by one Hund's case.

Examples. According to the above statements the most typical potential curves are those listed in Table 1. Transition from one case to another occurs of course step by step through intermediate cases.

I. The low vibrational states correspond to case "c", for the higher states the intermediate case between "c" and "e" may occur. An admixture of the case "e" is exponentially small if "e" takes place only at $R < p$ but it may be important if "e" penetrates into the $R > p$ region.

II. For small v's case "a" takes place. As v increases the transition to an intermediate case between "a" and "d" occurs, as happened for the "e" and "c" cases.

III. For small v case "b" occurs. As v goes up the case there may be either an intermediate case between "a" and "b" or mixed "a", "b", "d", or even an intermediate one between "a" and "d" (with a small admixture of "b"). The last would take place if the case "b" region is localized close to the potential energy minimum.

TABLE I

SOME POSSIBLE DISTRIBUTIONS OF HUND'S CASES WITH R (See Fig. 1)

	1	2	3
I	e	c	c
II	d	a	a
III	d	b	a

[a] The Roman numerals denote alternative types of potential curves.

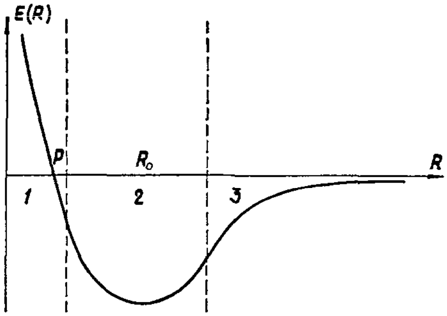

FIG. 1. The potential curve is divided into three regions with the one of Hund's cases predominating in each region. The most typical curves are listed in Table 1.

CONCLUSIONS

It has been shown that on the basis of nonempirical calculations using the equations proposed, molecules may be divided naturally into groups corresponding to certain Hund's cases to yield accurate description of their rotational spectra. A subsequent interpretation has been carried out for the changes of Hund's cases as the rotational or vibrational quantum number varies. Further development of this approach may result in more detailed understanding of the regularities as well as irregularities in the rotational spectra. An extension of this technique to polyatomic molecules is also possible.

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