

Correlation diagrams for Hund's coupling cases in diatomic molecules with high rotational angular momentum

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A diatomic molecule has in general three angular momenta: electronic orbital angular momentum \mathbf{L} , electronic spin angular momentum \mathbf{S} , and nuclear rotation angular momentum \mathbf{R} . They couple together to form the total angular momentum \mathbf{J} . Nuclear spin angular momentum \mathbf{I} , if present, usually couples to \mathbf{J} to form \mathbf{F} , but this coupling is ignored in this paper. In general, \mathbf{L} , \mathbf{S} , and \mathbf{R} are not conserved, whereas \mathbf{J} is. We consider the limit $J \gg L, S$, where angular momentum addition can be treated semiclassically. We present correlation diagrams that connect five limiting coupling cases (Hund's cases (a)–(e)) for a given value of J at a fixed internuclear separation r . The results pertain to bound states of a molecule as well as to two atoms 'in collision'.

1. Introduction

A stationary state of a system of two atoms in a bound or free (scattering) state is specified by a set of exact quantum numbers that may be related to the symmetry properties of the Hamiltonian \hat{H} that describes the motion of electrons and nuclei. These quantum numbers are the total energy E (because the total Hamiltonian does not depend on time), the square of the total angular momentum $J(J+1)$, the projection of \mathbf{J} onto the space-fixed quantization axis M (because the total Hamiltonian is invariant under an arbitrary rotation of the coordinates of electrons and nuclei), the total parity P (because the total Hamiltonian is invariant under the inversion of spatial coordinates of electrons and nuclei), and the transposition symmetry T of identical nuclei in the case of a homonuclear molecule (assuming that the hyperfine interaction in the total Hamiltonian is ignored). The set $n = E, J, M, P, T$ represents exact quantum numbers that enter into the electron–nuclear wavefunction $\Psi_n(\mathbf{r})$. Here \mathbf{r} stands for the vector that joins the two nuclei; as for the spatial and spin variables of electrons, they are not expressed explicitly.

The set of exact quantum numbers n is usually complemented with a set of good quantum numbers g that become additional exact quantum numbers in a certain limit of angular momentum coupling. The set n, g specifies a wavefunction $\Psi_{n,g}(\mathbf{r})$ that represents the first-order approximation to the exact wavefunctions $\Psi_n(\mathbf{r})$. By this statement we mean that a wavefunction $\Psi_n(\mathbf{r})$ can be expanded in the $\Psi_{n,g}(\mathbf{r})$

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as a complete basis set

$$\Psi_n(\mathbf{r}) = \sum_g F_{n,g} \Psi_{n,g}(\mathbf{r}), \quad (1)$$

with one coefficient, $F_{n,g}$, being on the order of unity, and all others much smaller than unity in their absolute values. The set of good quantum numbers g that makes the representation (1) valid, clearly depends on the interplay of different kinds of interactions that enter into the Hamiltonian. For a bound state of two atoms (a stable diatomic molecule), a set of good quantum numbers usually includes electronic quantum numbers. Different selections of such electronic quantum numbers form the five so-called Hund's coupling cases [1–4]. The situation becomes more complicated for the continuum states, because the scattering boundary conditions for these states are more versatile than the boundary conditions for the bound state. Nevertheless, the idea put forward by Hund in his pioneering paper [1] for bound states can be applied easily to the continuum states if, in place of an exact function $\Psi_n(\mathbf{r})$, consideration is given to its counterpart at a fixed internuclear distance r , $\Psi_n(\hat{\mathbf{r}}; r)$, where $\hat{\mathbf{r}}$ is a unit vector in the direction of the molecular axis [5, 6], and the dynamical variable $\hat{\mathbf{r}}$ is separated from the parameter r by a semicolon. Clearly the $\Psi_n(\hat{\mathbf{r}}; r)$ represent the wavefunctions of electrons and a rotating diatom at a fixed internuclear distance r , and they are eigenfunctions of the modified Hamiltonian, \hat{H}_{mod} , in which the kinetic energy term that corresponds to the radial motion of atoms is removed. We emphasize that the symmetry of the original Hamiltonian \hat{H} and that of the modified Hamiltonian \hat{H}_{mod} are the same. Because the functions $\Psi_n(\hat{\mathbf{r}}; r)$ describe the electronic motion in the field of the rotating rigid nuclear framework, they can be called *rotronic* (rotational–electronic) wavefunctions. The use of rotronic for rotational–electronic is in the same spirit as vibronic is used for vibrational–electronic, rovibrational for rotational–vibrational, and rovibronic for rotational–vibrational–electronic.

Similar to the representation (1) for the total wavefunction, two equations can be written, one relating the exact rotronic function $\Psi_n(\hat{\mathbf{r}}; r)$ to its zero-order counterparts $\Psi_{n,g}(\hat{\mathbf{r}}; r)$, and another expressing the total wavefunction in terms of zero-order rotronic functions:

$$\Psi_n(\hat{\mathbf{r}}; r) = \sum_g F_{n,g}(r) \Psi_{n,g}(\hat{\mathbf{r}}; r), \quad (2)$$

and

$$\Psi_n(\mathbf{r}) = \sum_g \Phi_{n,g}(r) \Psi_{n,g}(\hat{\mathbf{r}}; r). \quad (3)$$

In equation (2), r is a parameter and $\hat{\mathbf{r}}$ represents two dynamic variables. If, for a given r , only one coefficient in the sum in equation (2) is large, the corresponding zero-order rotronic function, say $\Psi_{n,g}(\hat{\mathbf{r}}; r)$, provides a good approximation to $\Psi_n(\hat{\mathbf{r}}; r)$ at this internuclear distance; this approximation corresponds to a particular Hund's coupling case at a given internuclear distance r for a set g . If two or more coefficients are comparable, the situation corresponds to an intermediate Hund's coupling case. The determination of the coefficients $F_{n,g}(r)$ amounts to the solution of a system of linear algebraic equations.

In equation (3), \mathbf{r} in $\Psi_n(\mathbf{r})$ represents three dynamic variables; r represents a dynamic variable in $\Phi_{n,g}(r)$ and a parameter in $\Psi_{n,g}(\hat{\mathbf{r}}; r)$. If only one coefficient in the sum (3) is large, the corresponding zero-order function, say $\Phi_{n,g}(r) \Psi_{n,g}(\hat{\mathbf{r}}; r)$,

provides a good approximation to $\Psi_n(\mathbf{r})$ in the whole region of nuclear motion. This approximation corresponds to a particular Hund's coupling case for a given state of the radial nuclear motion described by the radial wavefunction $\Phi_{n,g}(r)$. The determination of the functions $\Phi_{n,g'}(r)$ amounts to the solution of a system of coupled second-order differential equations.

When quantum numbers comprised by the set n as well as parameter r in equation (2) are varied, the coefficients $F_{n,g}(r)$ change, which implies a passage from one Hund's coupling case to another. This paper's aim is to describe the interconnection between pure Hund's coupling cases on the basis of the correlation diagrams of the rotronic states of a diatom. In doing so we assume that the rotational angular momentum of the nuclei is much larger than the orbital and spin angular momenta of the electrons. This condition, which is often met in practice, allows a simplification of the algebra of angular momentum addition and permits the derivation of simple expressions for the rotronic energy levels of a diatom for any of the pure Hund's coupling cases.

Our paper is organized as follows. Section 2 briefly describes the different Hund's coupling cases, and section 3 considers simplifications that arise in the vector addition scheme when one vector is much smaller than the two others. Under this condition we introduce the J -helicity representation, which allows us to replace the addition of vectors by the addition of (signed) scalars. In sections 4 and 5 the parity and the nuclear symmetry of rotronic states are discussed. Section 6 examines J -helicity good quantum numbers and the rotronic energies for different Hund's coupling cases, and section 7 outlines general rules for construction of the correlation diagrams and gives an example of a correlation diagram.

2. Hund's coupling cases

For a fixed distance between two atoms, r , the various Hund's cases are classified according to the relative strengths of three basic interactions present in the molecular Hamiltonian in the body-fixed (rotating) frame: first, coupling of the electronic orbital angular momentum \mathbf{L} to the molecular axis $\hat{\mathbf{f}}$ (interaction of an electrostatic nature, V_{el}), second, coupling between \mathbf{L} and electronic spin \mathbf{S} (spin-orbit interaction of a magnetic nature, V_{so}), and third, coupling of \mathbf{L} and \mathbf{S} to the total angular momentum \mathbf{J} (rotational or the Coriolis interaction, V_{rot}). When measured in terms of frequencies, these three interactions correspond roughly to first, the frequency of an electronic transition ω_{el} between molecular states that arise from a degenerate atomic state, second, the frequency of a fine-structure transition in a free atom ω_{so} , and third, the frequency of rotation of the molecular axis ω_{rot} . Within this qualitative estimate, ω_{so} does not depend on r , ω_{rot} is proportional to r^{-2} (at a fixed value of the orbital angular momentum \mathbf{R} of the nuclei), and the r dependence of ω_{el} is governed by the nature of the adiabatic molecular potential curves. At large internuclear distances, ω_{el} falls off usually much more quickly than ω_{rot} does. In what follows we ignore spin-spin interaction that can act, in principle, to couple \mathbf{S} directly to $\hat{\mathbf{f}}$.

The qualitative pattern of different Hund's cases corresponds to all possible hierarchies of the type 'strong-intermediate-weak' among the three interactions involved. Each hierarchy defines a sequence of coupling of appropriate angular momenta, that is, it determines a set of good quantum numbers g .

The total number of different hierarchies is $3! = 6$. \mathbf{L} and \mathbf{S} do not play exactly the same role, however. For instance, \mathbf{L} couples directly to $\hat{\mathbf{f}}$ whereas \mathbf{S} does not. Because of this behaviour, only five distinct angular momentum coupling cases result.

Table 1. Hund's coupling cases.^a

Hund's coupling case	V_{el}	V_{so}	V_{rot}
<i>a</i>	strong	intermediate	weak
<i>b</i>	strong	weak	intermediate
<i>c</i>	intermediate	strong	weak
<i>d</i>	intermediate	weak	strong
<i>e</i>	weak	intermediate	strong
<i>e'</i>	weak	strong	intermediate

^a Cases *e* and *e'* are degenerate because the good quantum numbers for these two cases are the same. It is traditional to adopt Hund's choice of case *e* and omit *e'*.

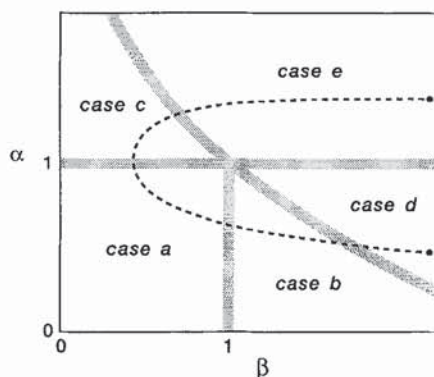


Figure 1. Different Hund's coupling cases in the $\alpha\beta$ plane, where $\alpha = \omega_{so}/\omega_{el}$ and $\beta = \omega_{rot}/\omega_{so}$. Points far away from the boundaries between different regions correspond to pure Hund's coupling cases, as indicated. Crossing of a boundary implies a change of the coupling case. The dashed line shows one of many possible paths for changing the coupling cases.

This conclusion will be clearer when the good quantum numbers are identified explicitly (see below). For the time being, we can list six coupling cases as shown in table 1.

Different Hund's coupling cases can be also displayed schematically as different regions in the plane of two variables $\alpha = \omega_{so}/\omega_{el}$ and $\beta = \omega_{rot}/\omega_{so}$, as shown in figure 1. Note that α strongly increases with increasing r (free-atom limit), and β is proportional to the total angular momentum.

3. Angular momenta of rotronic states

For a rotating diatomic system with a fixed internuclear distance, we consider the addition of the total electronic angular momentum \mathbf{j} (also called J_a ; see Herzberg [3], p. 226) and the nuclear orbital momentum \mathbf{R} to form the total angular momentum \mathbf{J}

$$\mathbf{j} + \mathbf{R} = \mathbf{J}. \quad (4)$$

In turn, \mathbf{j} is the sum of the electronic angular momentum \mathbf{L} and electronic spin \mathbf{S}

$$\mathbf{j} = \mathbf{L} + \mathbf{S}. \quad (5)$$

Substitution of (5) into (4) yields

$$\mathbf{S} + \mathbf{N} = \mathbf{J}, \quad (6)$$

where

$$\mathbf{N} = \mathbf{L} + \mathbf{R} \quad (7)$$

is the total orbital angular momentum of electrons and nuclei.

Each of the above five vectors, \mathbf{L} , \mathbf{S} , \mathbf{j} , \mathbf{R} , \mathbf{J} , is characterized by projections onto a space-fixed axis and onto the molecular axis. Let the projections of these vectors onto a space-fixed (SF) axis be L_z , S_z , j_z , R_z , J_z , and the projections onto the body-fixed (BF) molecular axis, L_z , S_z , j_z , R_z , J_z , be \tilde{L} , \tilde{S} , $\tilde{\Omega}$, 0 , $\tilde{\Omega}$, where the z axis is chosen to lie along \mathbf{r} . A signed projection is denoted by a superscript tilde. According to the conventional nomenclature, these quantum numbers should be called r -helicity quantum numbers. (The identities $R_z = 0$ and $J_z = \Omega$ follow from the fact that \mathbf{R} is perpendicular to \mathbf{r} and $J_z = j_z$.)

Traditionally Λ is defined as $|\tilde{L}|$ (Herzberg [3] equation (V.2)), but \tilde{S} is kept as a signed quantity denoted by Σ (Herzberg [3] equation (V.6)). The absolute values of $\tilde{\Omega}$ that can arise from the addition of \tilde{L} and \tilde{S} can be written as $\Omega = |\tilde{L} + \tilde{S}|$ (Herzberg [3] equation (V.7)). These definitions are incomplete, however, in that for some situations the same value of Ω may correspond to different states. For example, a ${}^4\Pi$ state in which $\Omega = 1/2$ may arise from $\tilde{L} = 1$ and $\tilde{S} = -1/2$, and $\tilde{L} = -1$ and $\tilde{S} = 3/2$. To distinguish such states we must introduce an additional quantum number Γ defined as $\Gamma = \Lambda\Sigma$. The quantum number Γ serves the same purpose as the seniority quantum number does in atomic spectroscopy [7].

Consider when J , R , $N \gg L$, S . In this limit all the vector addition coefficients simplify because they can be replaced by their asymptotic representations that are valid when two vectors are large. In particular, $3j$ symbols become the Wigner d functions (see Appendix). A very simple geometric interpretation exists for this simplification. Assume, for instance, that \mathbf{R} and \mathbf{j} add to form \mathbf{J} (figure 2). In the limit J , $R \gg j$, it can be easily seen from figure 2 that

$$J - R = j_J(1 + \kappa), \quad (8)$$

where the correction term κ is of the order of $\max(j_J/J, j^2/J^2)$. Therefore, to a first approximation with respect to the ratio j/J the quantity $J - R$ can be identified with j_J , which is the projection of \mathbf{j} onto \mathbf{J} . We call this approximation the J -helicity representation. In the J -helicity representation, the operators \hat{L}_z , \hat{S}_z , \hat{j}_z , \hat{R}_z , \hat{J}_z are associated with the quantum numbers L_J , S_J , j_J , R , J .

In the J -helicity representation, equations (4), (6), and (7) for the vector quantities become equations for scalar quantities:

$$j_J + R = J, \quad (9)$$

$$S_J + N = J, \quad (10)$$

and

$$N = L_J + R. \quad (11)$$

Equations (9) to (11) are the key to reducing the problem of addition of vectors to simply the addition of scalars.

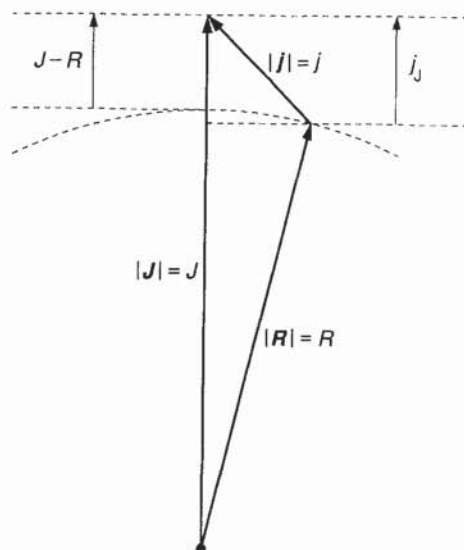


Figure 2. Addition of two vectors, \mathbf{R} and \mathbf{j} , to form \mathbf{J} under the condition $R, J \gg j$. This figure illustrates that the projection of \mathbf{j} onto \mathbf{J} (J helicity) is approximated by $J - R$ for large J .

4. Parity of rotronic states

The total parity quantum number P is the eigenvalue of the inversion operator \hat{P} that transforms the spatial coordinates of electrons and nuclei into the negative of themselves; by definition, the electron spin functions are invariant under this operation.

The two possible parity quantum numbers are $+1$ (*positive* states) and -1 (*negative* states). Spatial inversion P can be accomplished as a succession of two (commuting) operations: the rotation $C_2(\mathbf{v})$ through π about an arbitrary axis \mathbf{v} and the reflection $\sigma(\mathbf{v})$ in a plane normal to \mathbf{v} [8]:

$$P = C_2(\mathbf{v})\sigma(\mathbf{v}) = \sigma(\mathbf{v})C_2(\mathbf{v}). \quad (12)$$

Each symmetry operation on the right-hand side of equation (12) is exact if it is carried out in a space-fixed frame; therefore, the parity quantum number P can be related to other exact quantum numbers that correspond to rotation and reflection. If \mathbf{v} is taken to be directed along the Z axis of the SF frame, and if the sense of rotation is positive, equation (12) implies

$$P = \exp(iM\pi) \sigma_{rt}. \quad (13)$$

Here σ_{rt} is an exact quantum number of a specific rotronic state. Clearly, σ_{rt} is related to the parity quantum number P and the projection quantum number M . Because no property of an isotropic system depends on M , we are free to fix the value of M . We choose $M = J$ because this choice leads to a simple, appealing semiclassical identification for the direction of \mathbf{J} and for the meaning of σ_{rt} in the limit of high J values. Within this convention,

$$P = \exp(iJ\pi) \sigma_{rt}. \quad (14)$$

In the high- J limit, the rotronic quantum number σ_{ri} , defined according to equation (14), becomes the electronic quantum number σ_{el} , which specifies the symmetry of the electronic wavefunction under reflection of both the spatial and spin coordinates in the plane in which the nuclear framework rotates. Indeed, for large J , \mathbf{J} can be considered a classical vector with a fixed direction. The state $M = J$ corresponds to the situation in which \mathbf{J} is directed along the Z axis and the rotation of nuclei occurs in the XY plane. The semiclassical rotational wavefunction for this state looks like a pancake lying in the X, Y plane, and the reflection of the coordinates of the nuclei in this plane does not affect this state. (Classically, it follows that a reflection of two rotating atoms in the plane of rotation does not change the classical state of motion.) Thus, the semiclassical limit of equation (14) clearly assumes the form

$$P = \exp(iJ\pi) \sigma_{\text{el}}. \quad (15)$$

The difference between equations (14) and (15) in the structure of the wavefunctions yield an interesting conclusion. In the general case, when J is not large, a rotronic wavefunction that corresponds to definite quantum numbers J , M , and P does not factor into the product of nuclear and electronic parts, but it does factor in the limit $J \gg L, S$.

If J is an integer, $\exp(iJ\pi)$ assumes values ± 1 and so does σ_{el} . If J is a half integer, both $\exp(iJ\pi)$ and σ_{el} assume values $\pm i$. According to the nomenclature suggested in [9], we can make the following assignment of rotronic levels of different reflection symmetries to e and f labels:

If J is an integer,

levels with reflection symmetry $\sigma_{\text{el}} = 1$ are e levels, and
levels with reflection symmetry $\sigma_{\text{el}} = -1$ are f levels.

If J is a half integer,

levels with reflection symmetry $\sigma_{\text{el}} = -i$ are e levels, and
levels with reflection symmetry $\sigma_{\text{el}} = i$ are f levels.

Had we chosen the opposite sense of rotation through the angle π about \mathbf{J} , the reflection symmetry assignment of rotronic energy levels would have remained the same for integer values of J , but they would be reversed for half-integer values of J . This behaviour indicates that the reflection symmetry plays a different role for diatoms with integer and half-integer values of J . Indeed, if an external electric field is applied to a diatomic molecule, each Λ component of the Λ doublet will be split into Stark sublevels. For integer J , the pattern of the Stark sublevels will be different for e and f levels, whereas the two patterns will be the same if J is a half integer. Assume that the Coriolis coupling is vanishingly small. Then for integer values of J , the two Stark patterns will not coincide; for half-integer values of J , these patterns will coincide (superimpose) exactly. This behaviour is a manifestation of the Kramers degeneracy for half-integer values of angular momentum [4, 10], which follows from time-reversal symmetry. The Coriolis interaction lifts the Kramers degeneracy because the rotational coupling plays the role of a magnetic field.

If the spin is completely decoupled from $\hat{\mathbf{r}}$ arising from the fast rotation of the molecule, N is a good quantum number. A counterpart of equation (15) is then written as

$$P = \exp(iN\pi) \sigma'_{\text{el}}, \quad (16)$$

where the prime means that the reflection affects only the spatial coordinates of the electronic wavefunction. Because N is always an integer, σ'_{el} assumes values ± 1 . This is the case discussed in [11, 13]. According to the nomenclature suggested in [11], states with $\sigma'_{el} = 1$ are called A' states, and those with $\sigma'_{el} = -1$ are called A'' states.

Since J and N are related by equation (10) we have

$$\sigma_{el} = \exp(-iS_J\pi) \sigma'_{el}. \quad (17)$$

Equation (17) allows us to generalize the A' , A'' nomenclature to the cases in which the spin-orbit coupling is not small, and therefore the J -helicity quantum number S_J loses its meaning as a good quantum number. This generalization can be accomplished by the adiabatic variation of the magnitude of the spin-orbit coupling, that is, by the adiabatic passage from the Hund's case b to the Hund's case a . In identifying the A' and A'' levels, [11] considered the case in which the spin-orbit interaction becomes progressively smaller than the Coriolis interaction with increasing J . The present treatment does not require the spin-orbit interaction to be much smaller than the Coriolis interaction but does assume that J is sufficiently high that the semiclassical picture (figure 2) is valid.

Finally, we note that in discussing the symmetry properties of rovibronic levels of linear molecules, [12] introduced two different planes of reflection: one associated with vector \mathbf{J} and another with vector \mathbf{N} . Under the condition $J, N \gg j$ adopted here and within our approximation of J helicity, these two planes coincide and need not be distinguished.

5. Nuclear symmetry of rotronic states

If two nuclei are identical, an additional exact quantum number appears that is related to the symmetry of the total wavefunction with respect to transposition of the two nuclei. The eigenvalues, T , of the transposition operator \hat{T} are $+1$ (*symmetric* states denoted by s) and -1 (*antisymmetric* states denoted by a). Because of the different statistics of nuclei (bosons or fermions), T is related to the total spin of the two nuclei I , each possessing nuclear spin $I_A = I_B$. For instance, for ${}^4\text{He}_2$ ($I_A = I_B = 0$), $I = 0$, and only s states are allowed; for ${}^1\text{H}_2$ ($I_A = I_B = 1/2$), $I = 0$ for s states (*para*-hydrogen) and $I = 1$ for a states (*ortho*-hydrogen). The assignment of nuclear spin states to the different transposition states is important for determination of the correct statistical weight of a given rotronic state.

If the transposition of nuclei is supplemented with the inversion of electrons through the point C that bisects the distance between the two nuclei, the whole operation amounts to the spatial inversion of the entire molecular system

$$\hat{P} = \hat{T}\hat{w}, \quad (18)$$

where \hat{w} stands for the operation of inversion of the spatial coordinates of electrons through point C . Because \hat{P} and \hat{T} are exact symmetry operations, so is \hat{w} , although the 'electron inversion point' C is not fixed in space. The quantum number w assumes values $+1$ (*gerade* states denoted by g) and -1 (*ungerade* states denoted by u).

If the two nuclei are not identical but their charges are equal, w ceases to be an exact quantum number, but it is a good quantum number in the adiabatic approximation. For instance, for H_2 and D_2 , g and u states are completely independent, and therefore non-rotating H_2 and D_2 molecules do not possess a permanent dipole moment. For HD , the adiabatic electronic wavefunction possesses

definite parity with respect to the \hat{w} operation, which implies of course the absence of a permanent dipole moment. Adiabatic g and u states, however, can be mixed by the radial motion of nuclei (e.g., by vibrations of a stable molecule), and this mixing gives rise to a permanent dipole moment of the non-rotating molecule. Because the internuclear distance is fixed in the rotronic representation, g and u are good quantum numbers not only for identical nuclei but also for diatomic molecules made up of different isotopes of the same element.

Combining equation (18) with equations (15) and (16) we get:

$$\exp(iJ\pi) \sigma_{e1} = \exp(iN\pi) \sigma'_{e1} = Tw. \quad (19)$$

For a given rotronic state (N or J is fixed, and w is g or u) and a given transposition symmetry (T is a or s), equation (19) shows which reflection symmetry (σ'_{e1} or σ_{e1}) is allowed. If T , w , and σ'_{e1} (σ_{e1}) are given, equation (19) determines the allowed values of the angular momentum quantum number N (J).

6. J -helicity quantum numbers and rotronic energies for different Hund's cases

J -helicity quantum numbers for different Hund's coupling cases are established from the standard assignment [2, 3, 13] by correspondence between electronic quantum numbers and rotronic quantum numbers (see table 2 which shows that cases e and e' are degenerate, and that both can be united under the coupling case e).

A correlation between different Hund's cases is based on the rotronic Hamiltonian $\hat{H}(r)$, which reads

$$\hat{H}(r) = \hat{H}_{e1}(r) + \hat{\mathbf{R}}^2 \hbar^2 / 2mr^2, \quad (20)$$

where $\hat{H}_{e1}(r)$ is the electronic Hamiltonian for the non-rotating diatom, and $\hat{\mathbf{R}}^2 \hbar^2 / 2mr^2$ is the Hamiltonian for the rigid rotor. According to equations (4) through (7), we have

$$\mathbf{R} = \mathbf{J} - \mathbf{j} = \mathbf{N} - \mathbf{L} = (\mathbf{J} - \mathbf{L}) - \mathbf{S}. \quad (21)$$

The rotronic energy levels $E_{n,g}(r)$ for pure Hund's coupling cases are the expectation values of $\hat{H}(r)$ calculated with wavefunctions $\Psi_{n,g}(\hat{\mathbf{r}}; r)$, where the set g comprises good quantum numbers appropriate to one of the coupling cases. We

Table 2. Good electronic quantum numbers and the nomenclature of electronic states for different Hund's coupling cases at a fixed total angular momentum quantum number J .

Hund's coupling case	Good and (exact) quantum numbers ^a	Nomenclature of electronic states
a	$A, S, \Sigma; [\sigma'_{e1}, (w)]$	$^{2S+1}A_{\Omega,w} (A \neq 0);$
b	$A, S, S_J; [\sigma'_{e1}, (w)]$	$^{2S+1}A_w (A \neq 0); ^{2S+1}\Sigma_w^{\sigma'_{e1}} (A = 0)$
c	$\Omega [\sigma_{e1}, (w)]$	$\Omega_w (\Omega \neq 0); 0_w^{\sigma_{e1}} (\Omega = 0).$
d	$L, L_J, S, S_J; [\sigma'_{e1}, (w)]$	not established
e	$j, j_J; [\sigma_{e1}, (w)]$	not established
e'	$j, j_J; [\sigma_{e1}, (w)]$	

^a In case c if the diatom is composed of only one (high- Z) atom responsible for spin-orbit interaction, then j is a good quantum number.

represent $E_{n,g}(r)$ in the form

$$E_{n,g}(r) = U_{n,g}^{\text{el}}(r) + (J + 1/2)^2 \hbar^2 / 2mr^2 + \Delta E_{n,g}^{\text{rt}}(r). \quad (22)$$

where $U_{n,g}^{\text{el}}(r)$ is the adiabatic electronic energy, $(J + 1/2)^2 \hbar^2 / 2mr^2$ is the semiclassical energy of a rigid rotor possessing the angular momentum J , and $\Delta E_{n,g}^{\text{rt}}(r)$ is the first-order rotronic correction that arises from the Coriolis interaction \hat{V}_{rot} .

The adiabatic electronic energies depend on Λ for case b , Λ , and Σ (or Λ , $\Omega = |\hat{\Lambda} + \hat{\Sigma}|$ and Γ) for case a and on Ω for case c . No general formula for this dependence can be given unless a specific form of the electronic Hamiltonian is assumed. For illustration purposes we assume here that a diatom consists of an atom in a closed electronic shell (1S_0) and an atom in the electronic state $^{2S+1}L_J(p)$, where p is the parity of the atomic state ($p = +1$ for *even* states, $^{2S+1}L_J$; $p = -1$ for *odd* states, $^{2S+1}L_J^o$). To be specific, we take the case for which the atom in the 2P state arises from a single valence p electron so that the parity is $p = -1$.

The electronic Hamiltonian of a system of two atoms in the basis of the functions belonging to these states can be written as

$$\hat{H}_{\text{el}}(r) = V(r) + A(r)\mathbf{L} \cdot \mathbf{S}. \quad (23)$$

The Coriolis interaction has the form

$$\hat{V}_{\text{rot}} = -\dot{\phi}(\hat{L}_J + \hat{S}_J)\hbar, \quad (24)$$

where $\dot{\phi} = (J + 1/2)\hbar/mr^2$ is the angular velocity of the overall rotation, and \hat{L}_J , \hat{S}_J are the operators of the projections of the respective components of \mathbf{L} and \mathbf{S} onto \mathbf{J} .

Because the rotational energy in the J -helicity representation is the same for all coupling cases, we can discard the rotational energy when comparing rotronic energies for different coupling cases. In this way we arrive at table 3, which gives the electronic, spin-orbit, and Coriolis contributions to the rotronic energy levels for the five Hund's coupling cases.

The following comments on table 3 are in order. For Hund's cases a and b , the reflection symmetry quantum number σ'_{el} enters into the rotronic energy explicitly through the adiabatic electronic energies for states with $\Lambda = 0$ (Σ^+ and Σ^- states). For a homonuclear diatom for which the quantum number w exists, the reflection symmetry quantum number enters into these equations also implicitly through the constraint imposed by equation (19).

For the Hund's case c , the reflection symmetry σ_{el} enters into the rotronic energy explicitly through the adiabatic electronic energies for states with $\Omega = 0$ (0^+ and 0^- states) and through the Coriolis correction. Again, for a homonuclear diatom the

Table 3. Electronic, spin-orbit, and Coriolis contributions to the rotronic energy levels for the five different Hund's coupling cases.

Hund's coupling case	V_{el}	V_{so}	V_{rot}
a	$V_{\Lambda, \sigma'_{\text{el}}, w}(r)$	$A\Lambda\Sigma$	
b	$V_{\Lambda, \sigma'_{\text{el}}, w}(r)$		$-\dot{\phi}S_J\hbar$
c	$V_{\Omega, \sigma_{\text{el}}, w}(r)$		$\delta_{\Omega, 1/2} i\sigma_{\text{el}} \dot{\phi}(j + 1/2)\hbar/2$
d	$V_{L, S, L_J, w}(r)$	$AL_J S_J$	$-\dot{\phi}(L_J + S_J)\hbar$
e	$V_{j, j, w}(r)$		$-\dot{\phi}j\hbar$

quantum number σ_{el} enters into the rotronic energy also implicitly through the constraint imposed by equation (19).

For Hund's case *d*, the reflection symmetry quantum number σ'_{el} does not appear in table 3 because for this case (a Rydberg electron outside a core of a stable diatomic molecule [12] or almost free atoms [5]), the reflection is not an independent operation but is related to the inversion of the atomic wavefunctions. In the limit of large r , $V_{L,S,L_j,w}(r)$ becomes the energy of free atoms with the spin-orbit interaction neglected, $E(^1S_0) + E(^{2S+1}L(p))$.

For Hund's case *e*, the spin-orbit contribution in the limit of large r becomes identical to the spin-orbit interaction in a free atom, and in this limit the electronic contribution $V_{jj,w}(r)$ becomes the fine-structure energy levels of the free atoms $E(^1S_0) + E(^{2S+1}L_j(p))$. Again, similar to Hund's case *d*, σ_{el} does not appear explicitly in table 3.

Finally, we note that in a general case σ_{el} and σ'_{el} are expressed via $p = p_A p_B$ as

$$p = \exp(iL_J\pi) \sigma'_{el} = \exp(ij_J\pi) \sigma_{el}. \quad (25)$$

7. Correlation diagrams of rotronic energies between different Hund's cases

A correlation diagram for different Hund's coupling cases is a plot that connects rotronic energy levels in a prescribed sequence under conditions imposed by the non-crossing rule [3, 14]. For a given J , only one symmetry quantum number, the reflection symmetry, is exact for a heteronuclear diatom; for a homonuclear diatom, w is also exact. Therefore, the correlation diagram is readily constructed provided a particular path is chosen in the $\alpha\beta$ plane (figure 1). For instance, a path shown in figure 1 implies the sequence $d \rightarrow b \rightarrow a \rightarrow c \rightarrow e$. As an example, we consider a correlation diagram along this path for rotronic states that originate from $^1S_0 + ^2P_j^o$ atomic states.

First we discuss a simplified case in which the electronic spin is ignored. In this case, all the possible Hund's cases are either *d* or *b*. The three degenerate energy levels of a P state of a free atom are split into three equidistant components that correspond to quantum numbers $-1, 0, +1$ when an observer moves from the SF frame to the BF frame (in the BF frame a free atom looks like it is precessing with a frequency equal in magnitude but opposite in sign to the angular frequency of rotation of the frame). The energy levels are ordered in decreasing order of L_J , according to equation (24). The interatomic electrostatic interaction displaces slightly the positions of these levels; this situation is Hund's case *d*. The reflection symmetry σ'_{el} of a state specified by L_J is $(-1)^{1+L_J}$.

In case *b* we first plot the positions of the electronic energy levels (Σ^+ and Π states originate from a spinless P state that comes from a single valence p electron; reflection symmetry of the Σ state is $+1$, and that of Π state is $+1$ and -1). Direct application of the non-crossing rule yields graphs presented in figure 3. The splitting between the two lowest energy levels vanishes in pure Hund's case *b*; this splitting indicates the deviation from the pure Hund's case *b* and represents Δ doubling. According to the nomenclature indicated previously, we designate these levels A' and A'' .

Next we include spin-orbit interaction. For Hund's case *d*, we begin with a sixfold degenerate atomic energy level (three for the spatial degeneracy and two for spin), which in the rotating frame is split into four levels because of Coriolis interaction.

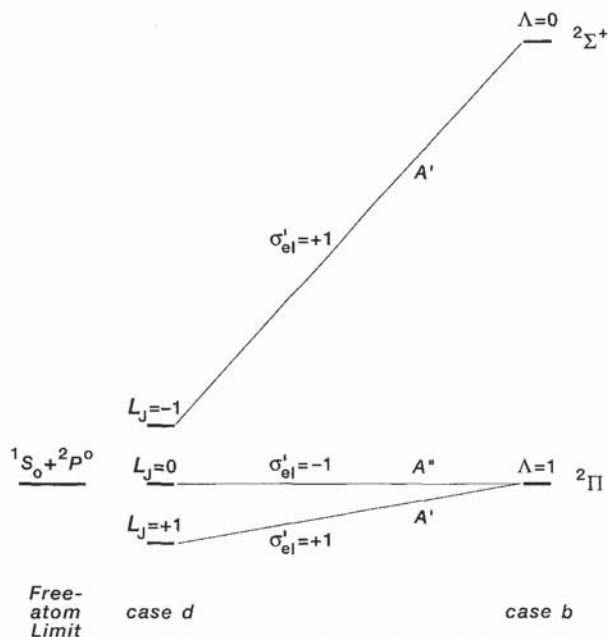


Figure 3. Correlation diagram between Hund's cases *d* and *b* for a diatom whose separated atoms approach the free-atom states $^1S_0 + ^2P^0$ in which the $^2P^0$ state arises from a single valence p electron. Electronic spin is ignored. Heavy lines correspond to electronic energy levels.

The upper and lower levels correspond to the negative and positive sums of L and S in the J -helicity representation. The two middle levels are doubly degenerate, and they correspond to different combinations of L_J and S_J . Actually, this degeneracy is removed by a very weak interatomic electrostatic interaction.

The rotronic energy levels for case *b* can be calculated from two electronic energy levels (one for a spinless Σ state and the other for a spinless Π state) by adding the spin-Coriolis interaction energy $-\hat{\phi}S_J\hbar$ (see equation (24)). Interpolation between case *d* and case *b* limits under the condition of the non-crossing rule yields the energy level pattern shown in figure 4. Actually, this pattern can be constructed from the diagram that completely neglects the existence of the electronic spin, followed by the up-and-down shift of the pattern. This correlation diagram again shows A doubling, and the assignment of the A components to A' and A'' states.

Passing from case *b* to case *a* means turning on the spin-orbit interaction so that it exceeds the rotational coupling. If Σ were a good quantum number for both electronic states, the rotronic energy levels would consist of three levels, $^2\Sigma_{1/2}^+$, $^2\Pi_{3/2}$, and $^2\Pi_{1/2}$. Two degenerate components of the $^2\Sigma_{1/2}^+$ state, with Σ equal to $1/2$ and $-1/2$, however, are coupled by the Coriolis interaction, which mixes this component to produce two S_J states. Analogous couplings between degenerate components of all non- Σ states vanish because of the special property of the rotronic wavefunctions for Hund's case *a*. This result is just another way to express that $^2\Sigma$ states always belong to Hund's case *b* (when spin-spin interaction is assumed to be negligible). The pattern of the rotronic energy levels for the Hund's case *a* is shown in the middle of figure 4.

Case *c* can be obtained from case *a* by decreasing the interatomic interaction

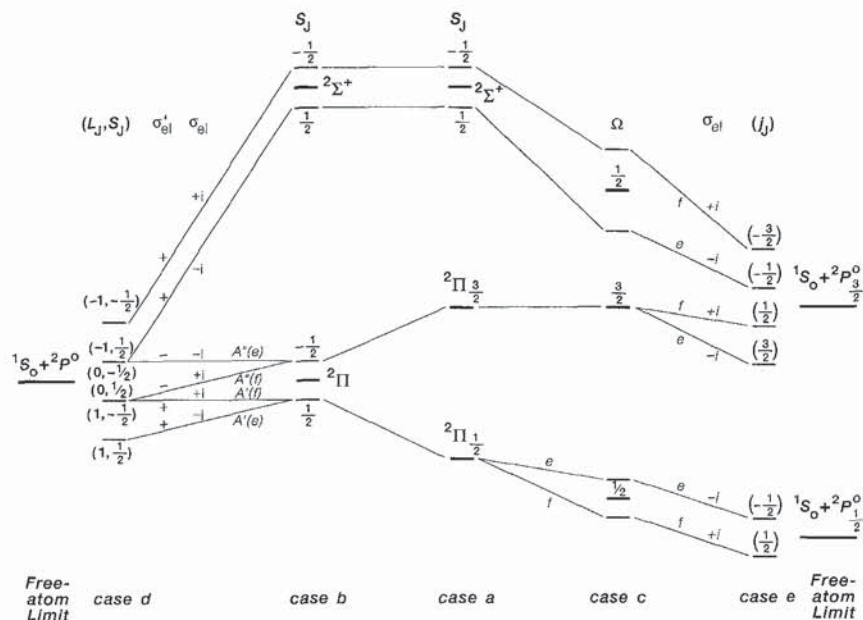


Figure 4. Correlation diagram between Hund's cases *d*, *b*, *a*, *c*, and *e* for a diatom whose separated atoms approach the free-atom states $^1S_0 + ^2P_j^o$ in which the $^2P_j^o$ state arises from a single valence p electron. Heavy lines correspond to electronic energy levels that include spin-orbit interaction as appropriate.

to the extent that $V_{cl} \ll V_{so}$. We see that Coriolis interaction splits the energy levels of $\Omega = 1/2$ but not those of $\Omega > 1/2$. In going from case *c* to case *a* the splitting of the $\Omega = 1/2$ doublet only disappears if $\Omega = 1/2$ correlates with a $^2\Sigma^+$ state. Finally, case *e* corresponds to the rotronic energy levels shown in the extreme right portion of figure 4. We collect in the Appendix the transformations of the electronic wavefunctions between all different Hund's coupling cases. These transformations simplify the construction of the correlation diagrams.

An interesting result that follows from figure 4 is the crossing of rotronic energy levels of different reflection symmetry along the correlation pattern. For instance, in the intermediate *d* – *b* case (left portion of figure 4), two lower levels correspond to *e* and *f* states, whereas the ordering is reversed in the intermediate *c* – *e* case. The spectroscopic manifestation of this crossing is the reversal of the regular parity pattern in a sequence of the *A*-doubled rotational levels of a diatomic molecule (e.g., $+-, -+, +- , \dots, +- , +- , -+, \dots$), where the increase in *J* results in a change of the coupling case. Another interesting feature can also be read from figure 4: the different qualitative behaviour of the *A*-doublet splitting as a function of the total angular momentum. The finite splitting in cases *d*, *e*, and *c* ($\Omega = 1/2$) implies that the splitting is proportional to the angular velocity $\dot{\phi}$, that is, to *J*. The splitting that vanishes in the limits of pure Hund's cases *b*, *a*, *c* indicates that the dependence of this splitting on *J* is of higher order.

The construction of the correlation diagram between different Hund's cases along a specific contour in the $\alpha\beta$ plane for this choice of atomic states is now complete. In a similar manner, correlation diagrams are readily constructed for other atomic

states. The same approach can be used for classification of rovibronic states of linear polyatomic molecules if the vibrational angular momentum is taken into account [12].

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Appendix

Asymptotic properties of vector addition

The semiclassical description of different Hund's coupling cases is based essentially on the following asymptotic behaviour of the Clebsch–Gordan coefficients for addition of two vectors, say \mathbf{R} and \mathbf{j} , to form the third \mathbf{J} under the condition $j \ll R, J$ [15, 16]:

$$(R, R_Z, j, j_Z | J, J_Z, R, j) = \delta_{j_Z - R_Z, j_Z} d_{j_Z, J-R}^j(\Theta), \quad (\text{A } 1)$$

where d is the Wigner d function [13], and Θ is the angle subtended by the vector \mathbf{J} and the Z axis, $\cos \Theta = J_Z/(J + 1/2)$.

Two obvious choices of representations for a diatom system bring equation (A 1) to a simpler form. The J -helicity representation assumes $J_Z = J$, i.e., $\Theta = 0$. In this case the Wigner rotation matrices become unit matrices:

$$d_{j_Z, J-R}^j(0) = \delta_{j_Z, J-R}. \quad (\text{A } 2)$$

The r -helicity representation assumes $J_Z = 0$, i.e., $\Theta = \pi/2$. In this case the d functions become the numerical elements of the so-called Δ matrix:

$$d_{j_Z, J-R}^j(\pi/2) = \Delta_{j_Z, J-R}^j. \quad (\text{A } 3)$$

The elements of the Δ matrix exhibit many useful symmetry properties and are tabulated for $1/2 \leq j \leq 5$ in [15] and numerically for $1/2 \leq j \leq 13$ in [17].

Consider the application of the asymptotic property (A 1) to simplify the Hund's coupling cases. The free-atom limit of a rotronic wavefunction $\Psi_{J,R,j}^{\text{rt}}$ in the J -helicity representation reads

$$\Psi_{J,R,j}^{\text{rt}} = \sum_{j_Z, R_Z} (R, R_Z, j, j_Z | J, J_Z, R, j) \Psi_{R,R_Z}^{\text{rot}} \Psi_{j,j_Z}^{\text{el}}, \quad (\text{A } 4)$$

where $\Psi_{R,R_Z}^{\text{rot}}$ is the wavefunction of the orbital relative motion of two atoms, and Ψ_{j,j_Z}^{el} is the electronic wavefunction. Using the asymptotic properties of the Clebsch–Gordan coefficients, equations (A 1) and equations (A 2), we get

$$\Psi_{J,R,j}^{\text{rt}} = \Psi_{R,R}^{\text{rot}} \Psi_{j,J-R}^{\text{el}}. \quad (\text{A } 5)$$

The position of the second subscript in Ψ^{el} identifies the difference $j_Z = J - R$ with the projection of \mathbf{j} onto \mathbf{J} (see section 3 and figure 2). Equation (A 5) can be rewritten in a form that contains the J -helicity quantum numbers

$$\Psi_{J,j,J}^{\text{rt}} = \Psi_{J-j,J-j}^{\text{rot}} \Psi_{j,j}^{\text{el}}. \quad (\text{A } 6)$$

The semiclassical factorization, equations (A 5) or (A 6), of the (non-separable) rotronic wavefunction, equation (A 4), into the nuclear and electronic parts allows passage from the addition of vectors to the addition of scalars (see section 3).

Because the rotronic function is factored into a nuclear and an electronic part, treating the dynamics of these two subsystems on two different levels of approximation poses no difficulty: the overall rotation is classical, and electronic motion is quantal. Moreover, all the transformations pertinent to different coupling cases are applied to the electronic wavefunctions only.

Different Hund's coupling cases exhibit no unique relation between electronic wavefunctions because all the interactions are different. Within the basis set belonging to one electronic state (fixed values of S, L), however, a unique relation exists between the set of wavefunctions $\Psi_{n,g}$ for a given pure Hund's case specified by the good quantum numbers g and the same set $\Psi_{n,(g),g'}$ expressed in terms of the quantum numbers of a different Hund's case (we call this the g -to- g' transformation). Showing that the following relations hold is easy:

(i) d-to-b transformation:

$$|L, L_J, S, S_J\rangle = \sum_{\tilde{\lambda}} \Delta_{L_J, \tilde{\lambda}}^L |L, \tilde{\lambda}, S, S_J\rangle, \quad (\text{A } 7)$$

(ii) b-to-a transformation:

$$|L, \tilde{\lambda}, S, S_J\rangle = \sum_{\Sigma} \Delta_{S_J, \Sigma}^S |L, \tilde{\lambda}, S, \Sigma\rangle, \quad (\text{A } 8)$$

(iii) a-to-c transformation:

$$|L, \tilde{\lambda}, S, \Sigma\rangle = |L, S, \Omega, \Gamma\rangle, \quad (\text{A } 9)$$

where $\Omega = |\Lambda + \Sigma|$ and $\Gamma = \Lambda\Sigma$, and

(iv) c-to-e transformation:

$$|j, \tilde{\Omega}\rangle = \sum_{j_J} \Delta_{j_J, \tilde{\Omega}}^j |j, j_J\rangle. \quad (\text{A } 10)$$

The chain of transformations (A 7) to (A 10) is complete if it is supplemented with the vector addition relations between \mathbf{L}, \mathbf{S} and \mathbf{j} :

$$|j, j_J\rangle = \sum_{L_J, S_J} (L, L_J, S, S_J | j, j_J, L, S) |L, L_J, S, S_J\rangle. \quad (\text{A } 11)$$

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