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Diatomic molecule nuclear motion problem:

$$\{-(\hbar^2/2M_A)\nabla^2_A -(\hbar^2/2M_B)\nabla^2_B + U_{\lambda,etc}(R)\}\Psi_{\text{nuclear motion}} = E\Psi_{\text{nuclear motion}}$$

Treat this ***just like the H atom problem***.

(1) Change from two-particle problem to an effective one-particle problem by using instead of (X_A, Y_A, Z_A, X_B, Y_B, Z_B) the set of coordinates

(a) (X_{CM}, Y_{CM}, Z_{CM}) with respect to the laboratory-fixed frame, with associated mass $M_{total} = M_A + M_B$ and

(b) (R,θ,ϕ) where R is R_{AB}, and θ and ϕ are with respect to the laboratory frame, except that the origin is translated to the center of mass of the diatomic molecule, with associated reduced mass μ, such that

$1/\mu = 1/M_A + 1/M_B$

and then using ***separation of variables*** to separate the problem in CM coordinates from the problem in internal motion coordinates.

Separation of variables leads to

$\Psi_{\text{nuclear motion}} =$

$$\Psi_{\text{transl}}(X_{CM}, Y_{CM}, Z_{CM}) \bullet \Psi_{\text{internal}}(R, \theta, \phi)$$

$E = E_{\text{transl}} + E_{\text{internal}}$

and two equations to solve,

$$\{-(\hbar^2/2M_{\text{total}})\nabla^2_{CM}\}\Psi_{\text{transl}} = E_{\text{transl}}\Psi_{\text{transl}} \qquad (1a)$$

$$\{-(\hbar^2/2\mu)\nabla^2_{R\theta\phi} + U_{\lambda,\text{etc}}(R)\}\Psi_{\text{internal}}$$
$$= E_{\text{internal}}\,\Psi_{\text{internal}} \qquad (1b)$$

(2) Separation of variables in solving eq.(1b) is again just like that in H atom, since ϕ can be separated out first, and then θ can be separated out next, leading to

$$\Psi_{\text{internal}} = \Psi_{\text{vib-rot}} = F(R) \bullet Y_{JM}(\theta, \phi).$$

Since eq. (1b) is identical to that of the H atom except that

instead of $-Ze^2/r$ we have $U_{\lambda,\text{etc}}(R)$,

$Y_{JM}(\theta,\phi)$ are the identical spherical harmonics functions and the rotational angular momentum quantum numbers J, M are the analogs of ℓ and m_ℓ.

(3) The R part that remains to be solved is

$$-(\hbar^2/2\mu)\{ d^2F/dR^2 + (2/R)dF/dR\} + J(J+1)\hbar^2F/2\mu R^2 + U_{\lambda,etc}(R)F = E_{elec\text{-}vib\text{-}rot}F$$

Just as in the H atom, we change variables:

$$G(R) = R \bullet F(R)$$

leading to

$$-(\hbar^2/2\mu)d^2G/dR^2 + J(J+1)\hbar^2G/2\mu R^2 + U_{\lambda,etc}(R)G = E_{elec\text{-}vib\text{-}rot}G \qquad (3)$$

Since the potential energy functions $U_{\lambda,etc}(R)$ have different shapes characteristic of the electronic state, we use a Taylor series expansion around $R=R_{eq}$ to represent the U(R) functions:

Let $x = R- R_{eq}$,

$$U_{\lambda,etc}(R) = U_{\lambda,etc}(R_{eq}) + (dU/dx)_0x + (1/2!)(d^2U/dx^2)_0x^2 + (1/3!)(d^3U/dx^3)_0x^3 + (1/4!)(d^4U/dx^4)_0x^4 + \ldots$$

where we note that $(dU/dx)_0 = 0$ since R_{eq} corresponds to the minimum of the $U_{\lambda,etc}(R)$ function.

and replace G(R) by S(x), so that the equation to be solved is now

$$-(\hbar^2/2\mu)d^2S/dx^2 + J(J+1)\hbar^2S/[2\mu(R_e+x)^2]$$
$$+ \{(1/2!)(d^2U/dx^2)_0x^2 + (1/3!)(d^3U/dx^3)_0x^3$$
$$+ (1/4!)(d^4U/dx^4)_0x^4 + \ldots\}S$$
$$= \{E_{\text{elec-vib-rot}} - U_{\lambda,\text{etc}}(R_e)\}S \qquad (4)$$

We can further replace the second term with its series expansion in powers of x:

$$[R_e^2/(R_e+x)^2] = 1 - 2x/R_e + 3x^2/R_e^2 + \ldots$$

so that the equation to be solved becomes:

$$-(\hbar^2/2\mu)d^2S/dx^2$$
$$+\{[-2x/R_e + 3x^2/R_e^2+\ldots]J(J+1)\hbar^2/2\mu R_e^2$$
$$+ (1/2!)(d^2U/dx^2)_0x^2 + (1/3!)(d^3U/dx^3)_0x^3$$
$$+ (1/4!)(d^4U/dx^4)_0x^4 + \ldots\}S$$
$$= \{E_{\text{elec-vib-rot}} - U_{\lambda,\text{etc}}(R_e) - J(J+1)\hbar^2/2\mu R_e^2\}S$$

The problem

$$-(\hbar^2/2\mu)d^2\Psi(x)/dx^2 + (1/2!)(d^2U/dx^2)_0x^2\Psi(x) = E_{HO}\Psi(x)$$

is a known QM problem which is exactly solvable. Therefore we can use perturbation theory to solve eq. (4) where $\mathcal{H} = \mathcal{H}^{(0)} + \boldsymbol{h}$ in which

$\mathcal{H}^{(0)} = -(\hbar^2/2\mu)d^2/dx^2 + (1/2!)(d^2U/dx^2)_0 x^2$

and HO(x) are the zeroth order wavefunctions, and

$$h = [-2x/R_e + 3x^2/R_e^2 + \ldots]J(J+1)\hbar^2/2\mu R_e^2 + (1/3!)(d^3U/dx^3)_0 x^3 + (1/4!)(d^4U/dx^4)_0 x^4 + \ldots$$

Write this so as to represent the constants in simpler form:

$h = ex + bx^2 + cx^3 + dx^4 + \ldots$

where, $e \equiv -2J(J+1)\hbar^2/2\mu R_e^3$

$b \equiv +3J(J+1)\hbar^2/2\mu R_e^4$

$c \equiv (1/3!)(d^3U/dx^3)_0$

$d \equiv (1/4!)(d^4U/dx^4)_0$

We can set up the matrix representation of h in the complete orthonormal set of HO(x) functions.

First we need the matrix representation of x, then by matrix multiplication and definition of matrix representation we will find the matrix representation of $h = ex + bx^2 + cx^3 + dx^4 + \ldots$

The matrix representation of x in the basis of the complete orthonormal set of harmonic oscillator eigenfunctions $\{\varphi_0 , \varphi_1 , \varphi_2 , \varphi_3 , \ldots\}$ is given by: (where $a = \hbar/4\pi\nu_e\mu$), and the corresponding energy eigenvalues are $(v+½)\hbar\nu_e$, where v = 0,1,2,3,…

$$x = a^{1/2} \begin{array}{|c|c|c|c|c|c|} \hline 0 & \sqrt{1} & 0 & 0 & 0 & \ldots \\ \hline \sqrt{1} & 0 & \sqrt{2} & 0 & 0 & \ldots \\ \hline 0 & \sqrt{2} & 0 & \sqrt{3} & 0 & \ldots \\ \hline 0 & 0 & \sqrt{3} & 0 & \sqrt{4} & \ldots \\ \hline \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \hline \end{array}$$

$$x^2 = a \begin{array}{|c|c|c|c|c|c|c|c|c|} \hline 1 & 0 & \sqrt{2} & 0 & 0 & 0 & 0 & 0 & \ldots \\ \hline 0 & 3 & 0 & \sqrt{6} & 0 & 0 & 0 & 0 & \ldots \\ \hline \sqrt{2} & 0 & 5 & 0 & \sqrt{12} & 0 & 0 & 0 & \ldots \\ \hline 0 & \sqrt{6} & 0 & 7 & 0 & \sqrt{20} & 0 & 0 & \ldots \\ \hline 0 & 0 & \sqrt{12} & 0 & 9 & 0 & \sqrt{30} & 0 & \ldots \\ \hline \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \hline \end{array}$$

$$x^4 = a^2 \begin{array}{|c|c|c|c|c|c|c|c|c|} \hline 3 & 0 & 6\sqrt{2} & 0 & \sqrt{24} & 0 & 0 & 0 & \ldots \\ \hline 0 & 15 & 0 & 10\sqrt{6} & 0 & \sqrt{120} & 0 & 0 & \ldots \\ \hline 6\sqrt{2} & 0 & 39 & 0 & 14\sqrt{12} & 0 & \sqrt{360} & 0 & \ldots \\ \hline 0 & 10\sqrt{6} & 0 & 75 & 0 & 18\sqrt{20} & 0 & \sqrt{840} & \ldots \\ \hline \sqrt{24} & 0 & 14\sqrt{12} & 0 & 123 & 0 & \sqrt{1680} & 0 & \ldots \\ \hline \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \hline \end{array}$$

$$E_v^{(0)} = (v+\tfrac{1}{2})\hbar\nu_e$$

$$E_v^{(1)} = b\,(\chi^2)_{v\,v} + d\,(\chi^4)_{v\,v} \quad [\text{since } (\chi^{\text{odd}})_{v\,v} = 0]$$

$$E_v^{(2)} = -\sum\nolimits_{k\neq v} \frac{\langle k|\,\boldsymbol{h}|v\rangle\langle v|\,\boldsymbol{h}|k\rangle}{E_k^{(0)} - E_v^{(0)}}$$

$$= -\sum\nolimits_{k} \frac{e^2(\chi_{k\,v})^2 + c^2(\chi^3_{\;k\,v})^2 + 2ec\,(\chi_{k\,v})(\chi^3_{\;k\,v})}{E_k^{(0)} - E_v^{(0)}}$$

in which we show only terms in $ex + cx^3$ [which are zero by symmetry in $E_v^{(1)}$ but which can contribute values of same order of magnitude as those in $E_v^{(1)}$]

$$E_{\text{elec-vib-rot}} = U_{\lambda,\text{etc}}(R_e) + J(J+1)\hbar^2/2\mu R_e^2 + E_v^{(0)} + E_v^{(1)} + E_v^{(2)}$$

$$\chi_{k\,v} = (2a)^{-1/2}\{v^{1/2}\delta_{k,v-1} + k^{1/2}\delta_{k,v+1}\}$$

$$(\chi^2)_{k\,v} = (2a)^{-1}\{(2v+1)\delta_{k,v} + v^{1/2}(v-1)^{1/2}\,\delta_{k,v-2} + (v+1)^{1/2}\,(v+2)^{1/2}\,\delta_{k,v+2}\}$$

$$(\chi^3)_{k\,v} = (2a)^{-3/2}\{\,3v^{3/2}\delta_{k,v-1} + 3(v+1)^{3/2}\delta_{k,v+1} + (v+1)^{1/2}(v+2)^{1/2}(v+3)^{1/2}\delta_{k,v+3} + v^{1/2}(v-1)^{1/2}(v-2)^{1/2}\delta_{k,v-3}\}$$

$$(\chi^4)_{v\,v} = (2a)^{-2}\{3v^2 + 3(v+1)^2\}$$

We see that $E_v^{(1)}$ has a dependence on both J(J+1) and $(v+½)\hbar\nu_e$ in the *b* term, and on $[(v+½)\hbar\nu_e]^2$ in the *d* term. On the other hand $E_v^{(2)}$ has a dependence on $[J(J+1)]^2$ in the e^2 term and $[(v+½)\hbar\nu_e]^2$ in the c^2 term, and has a dependence on both J(J+1) and $(v+½)\hbar\nu_e$ in the *ec* term. From these alone, one can recognize the perturbation terms that contribute to the spectroscopic constants that appear with $J(J+1)\bullet(v+½)\hbar\nu_e$, $[J(J+1)]^2$, $[(v+½)\hbar\nu_e]^2$, and other terms we chose not to evaluate in $E_v^{(2)}$ such as $[(v+½)\hbar\nu_e]^3(d^2)$, $[J(J+1)]^2\bullet(v+½)\hbar\nu_e(b^2)$, $J(J+1)\bullet[(v+½)\hbar\nu_e]^2(bd)$.

Thus, we can find the spectroscopic constants α_e $(b+ec)$, D_e (e^2), $\hbar\nu_e x_e$ $(d+c^2)$, $\hbar\nu_e y_e$ (d^2) , β_e (b^2), γ_e (bd), etc., in terms of the molecular constants $(d^3U/dx^3)_0$, $(d^4U/dx^4)_0$, [in addition to R_e and $(d^2U/dx^2)_0$ that the zeroth order rigid rotor+HO energies provide].

$$\begin{aligned} E_{\lambda,v,J} = {} & U_{\lambda,\mathrm{etc}}(R_e) \\ & + J(J+1)[\, B_e + \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + ..] \\ & + [J(J+1)]^2[\, D_e + \beta_e(v+\tfrac{1}{2}) + ..] \\ & + \hbar\nu_e(v+\tfrac{1}{2}) + \hbar\nu_e x_e(v+\tfrac{1}{2})^2 + \hbar\nu_e y_e(v+\tfrac{1}{2})^3 + .. \\ & + Y_{00} \end{aligned} \tag{5}$$

where, ***in energy units***,

$B_e \equiv \hbar^2/2\mu R_e^2$

$\hbar\nu_e \equiv \hbar\,[U''(R_e)/\mu]^{1/2}$

$D_e \equiv 4B_e^3/(\hbar\nu_e)^2$

$\alpha_e \equiv -2B_e^2/\hbar\nu_e \bullet \{3 + 2B_e[R_e^3 U'''(R_e)]\,/(\hbar\nu_e)^2\,\}$

$\hbar\nu_e x_e \equiv \tfrac{1}{4}B_e^2/(\hbar\nu_e)^2 \bullet \{(^{10}/_3)B_e[R_e^3 U'''(R_e)]^2/(\hbar\nu_e)^2 - [R_e^4 U^{iv}(R_e)]\,\}$

$Y_{00} \equiv (^1/_{16})B_e^2/(\hbar\nu_e)^2 \bullet \{-(^{14}/_9)B_e[R_e^3 U'''(R_e)]^2/(\hbar\nu_e)^2 + [R_e^4 U^{iv}(R_e)]\,\}$

Note that Y_{00} is the same anharmonic correction to every vibrational level. Y_{00} is a constant for the electronic state, so is usually put together with the electronic energy $U_{\lambda,\mathrm{etc}}(R_e)$. Note that purely electronic $U_{\lambda,\mathrm{etc}}(R_e)$ is mass-independent, while Y_{00} is not.

Signs:

We have written all the energy terms with + signs. In some books explicit negative signs are used in the energy expression so that all spectroscopic constants have positive values. The spectroscopic constants in eq. (5) that have negative values are $\hbar\nu_e x_e$, α_e , and D_e .

$U''(R_e) > 0$ always. With rare exceptions,

$$U'''(R_e) < 0 \text{ and } U^{iv}(R_e) > 0$$

Mass dependence:

Spectroscopic constants differ for isotopomers Examining the μ dependence of the constants, we find

$B_e \propto \mu^{-1}$

$\hbar\nu_e \propto \mu^{-1/2}$

$D_e \propto \mu^{-2}$

$\alpha_e \propto \mu^{-3/2}$

$\hbar\nu_e x_e \propto \mu^{-1}$

$Y_{00} \propto \mu^{-1}$

General shape of *U(x)*

(a) Morse function

$U(x) = \boldsymbol{D_e}\{1 - e^{-ax}\}^2$ in the dissociation energy $\boldsymbol{D_e}$, Morse parameter a

(b) As graduate students, Dudley Herschbach and Victor Laurie, discovered that force constants correlate with position of the atoms in the Periodic Table, i.e., in the potential function $U(x)$, $x = R-R_e$:

$U(x) = U(R_e) + \frac{1}{2}\{F_2x^2 + F_3x^3 + F_4x^4 \ldots\}$

for the ground electronic state of diatomic molecules, the empirical relation holds,

$$\boxed{(-1)^n F_n = 10^{-(R_e-a_n)/b_n}}$$

in which a_2 and b_2, a_3 and b_3, a_4 and b_4 , are ***the same for atoms in the same rows of the Periodic Table***.

[J. Chem. Phys. **35**,458(1961)]

Herschbach–Laurie parameters.

Row		a_2	a_3	b_2	b_3	Row		a_2	a_3	b_2	b_3
H	1	1.54	1.58	0.64	0.48	2	4	2.63	2.70	0.96	0.73
H	2	1.80	1.85	0.69	0.59	2	5	2.71	2.81	1.09	1.09
H	3	1.98	2.01	0.95	0.74	3	3	2.70	2.77	1.12	0.89
H	4	2.08	2.07	0.96	0.74	3	4	2.66	2.76	1.48	1.19
H	5	2.06	2.12	0.78	0.90	3	5	2.73	2.83	1.31	1.05
1	1	1.73	1.78	0.47	0.39	4	4	2.85	2.95	0.94	0.70
1	2	2.02	2.10	0.53	0.48	4	5	2.84	2.93	1.09	0.78
1	3	2.15	2.26	0.60	0.55	H	3T	1.82	1.92	1.04	0.86
1	4	2.36	2.41	0.76	0.57	H	4T	1.83		0.75	
1	5	2.47	2.48	0.87	0.68	H	5T	1.77		0.47	
2	2	2.40	2.48	0.70	0.61	1	3T	1.98		0.44	
2	3	2.54	2.57	0.98	0.72	1	4T	2.15		0.52	

Anharmonic potentials for diatomic molecules, $x \equiv R - R_e$, move energy zero to $U(R_e)$

Morse Potential

$$U(x) = D_e \left\{ 1 - \exp^{-ax} \right\}^2$$

Taylor series expansion:

$$U = \frac{1}{2!} U''(R_e)\, x^2 + \frac{1}{3!} U'''(R_e)\, x^3 + \frac{1}{4!} U^{iv}(R_e)\, x^4 + \dots$$

Morse potential $a \equiv$ Morse parameter

$$U''(R_e) = 2a^2 D_e$$

$$U'''(R_e) = -6a^3 D_e = -3a_{(3)} U''(R_e)$$

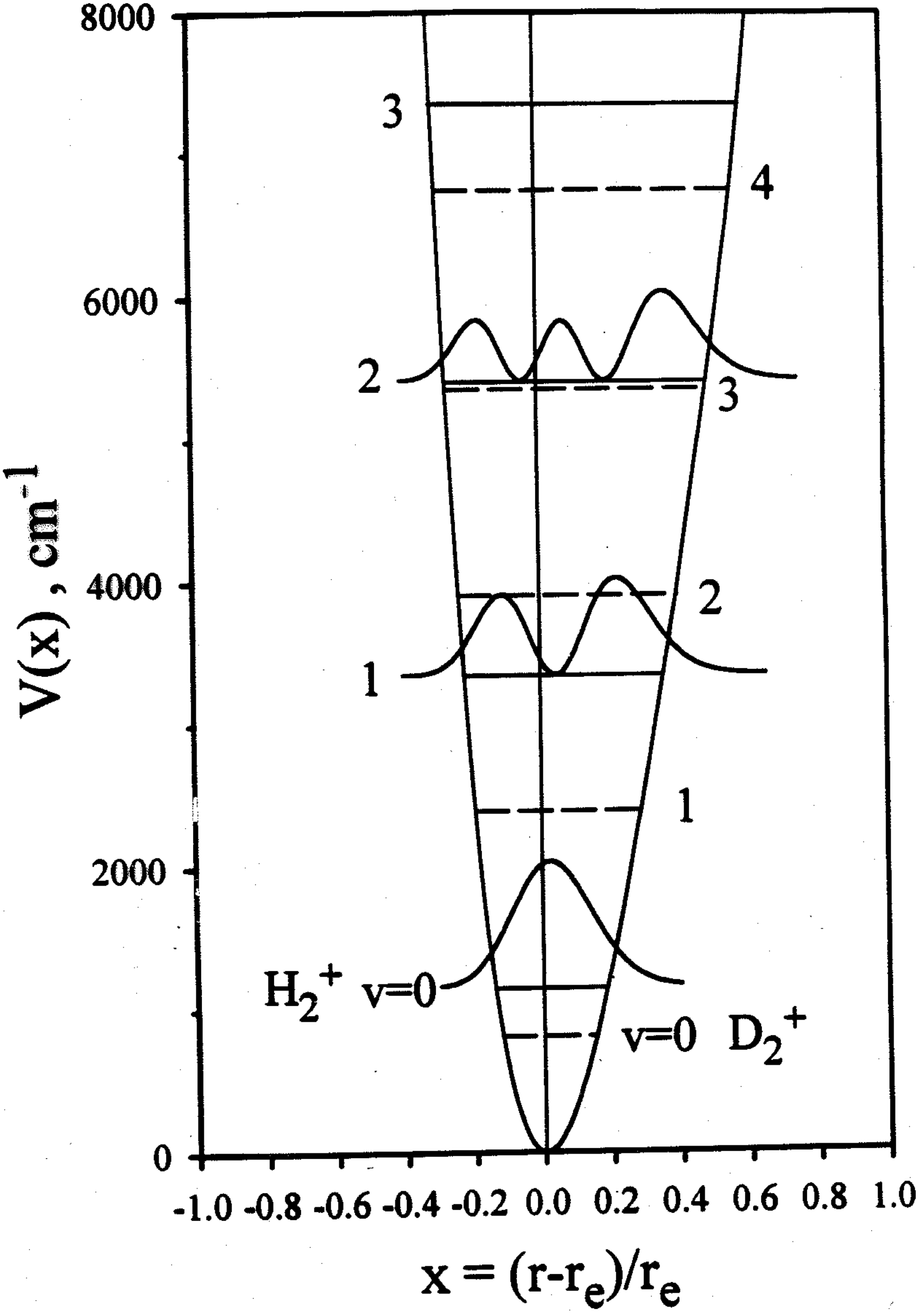
$$U^{iv}(R_e) = +10a^4 D_e = +7a_{(4)}^2 U''(R_e)$$

Given $U'''(R_e)$ and $U^{iv}(R_e)$ are known, can find Morse parameters $a_{(3)}$ (based on $U'''(R_e)$) and $a_{(4)}$ (based on $U^{iv}(R_e)$)

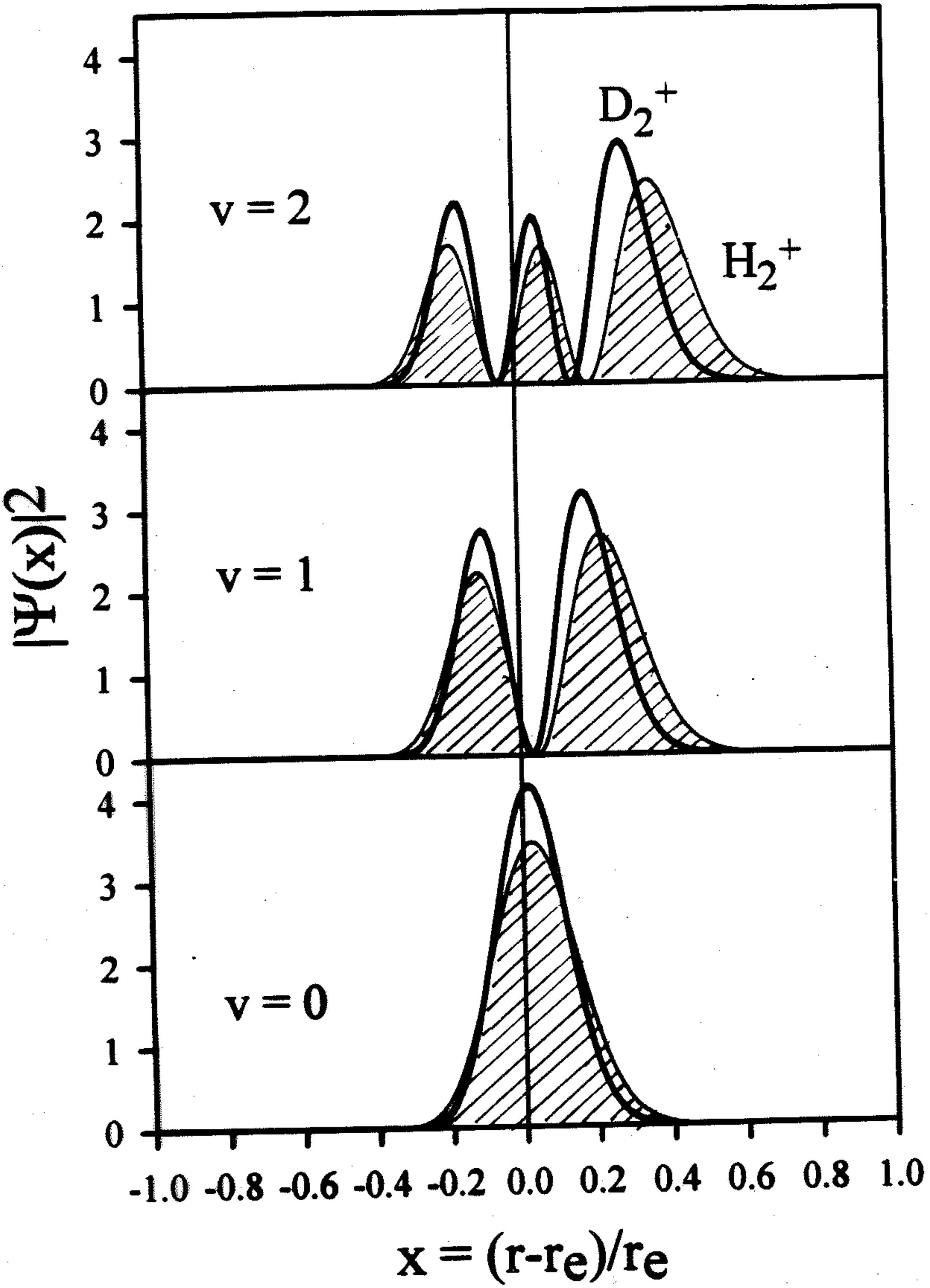
See Tables of $a_{(3)}$ $a_{(4)}$ ν_e x_e R_e in "Theoretical Chemistry, Specialist Periodical Reports" vol 1, 110 (1974)

For a Morse potential

$$D_e = \frac{-\omega_m^2}{4x_m} \quad \text{where } G(v) = \omega_m\left(v + \tfrac{1}{2}\right) + x_m\left(v + \tfrac{1}{2}\right)^2$$



8000
6000
4000
2000
0
V(x) , cm^{-1}
-1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0
x = (r-r$_e$)/r$_e$
3
4
2
3
2
1
1
H$_2^+$ v=0
v=0 D$_2^+$



$|\Psi(x)|^2$
v = 2
v = 1
v = 0
D_2^+
H_2^+
0
1
2
3
4
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0
$x = (r-r_e)/r_e$

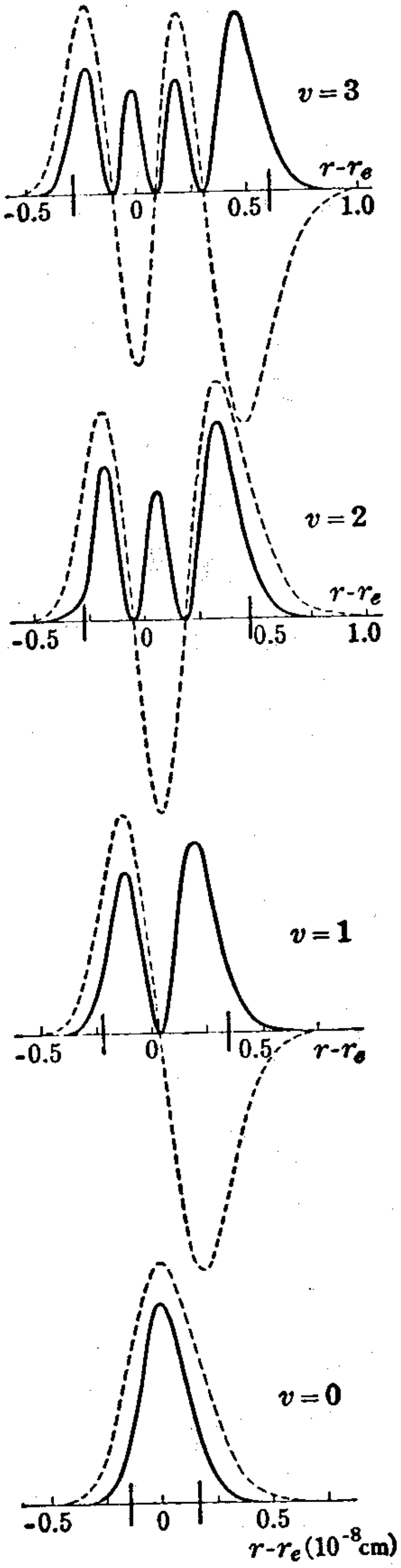


FIG. 48. Eigenfunctions (Broken Curves) and Probability Density Distributions (Solid Curves) of an Anharmonic Oscillator

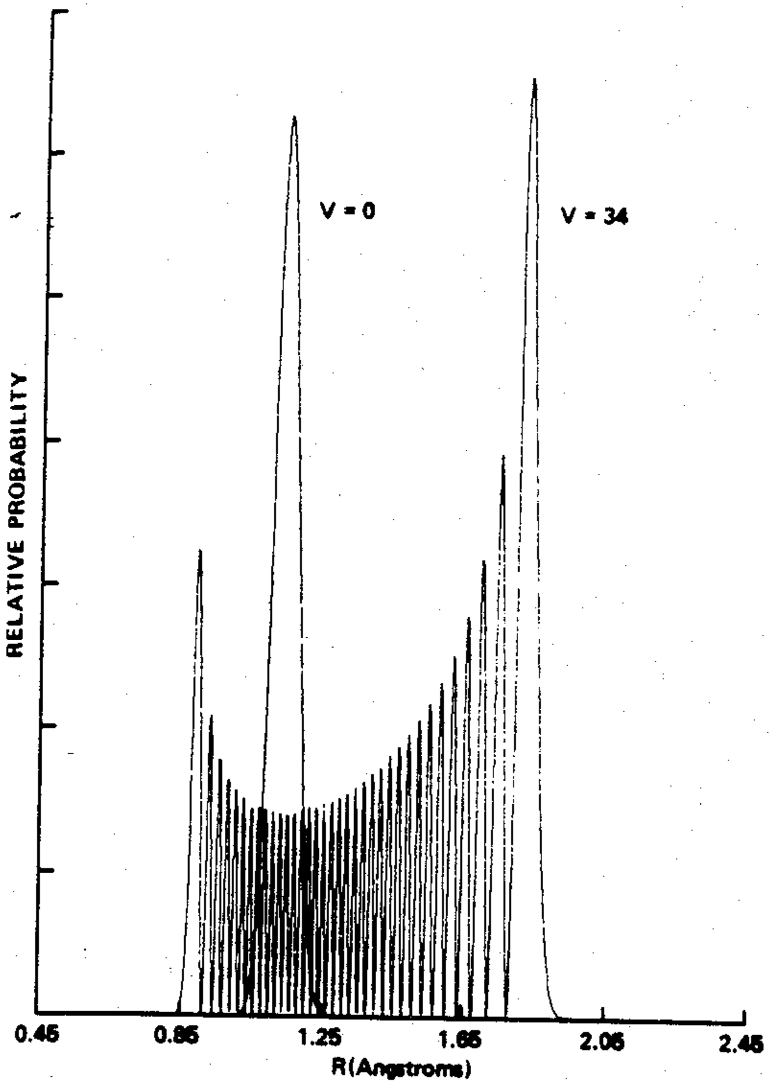


FIG. 1. Probability amplitude for nuclear position in the $V = 0$ and $V = 34$ vibrational states. For proper relative scaling multiply the vertical component of the $V = 0$ graph by 2.5. CO molecule

from Can. J. Phys. 62, 1579 (1984)

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SUMMARY OF SYMMETRY PROPERTIES OF MOLECULAR FUNCTIONS of DIATOMICS

$$\Psi_{total} = \psi_{\substack{elec.\\ space}} \times \psi_{\substack{elec.\\ spin}} \times \psi_{vib.} \times \psi_{rot.} \times \psi_{\substack{nucl.\\ spin}} \times \psi_{transl.}$$

OPERATION

I inversion of <u>all</u> <u>space</u>-fixed coords.

$$I\,\Psi_{total} = \pm\,\Psi_{total}$$

total <u>parity</u> is + or −

$$I\,\psi_{rot} = (-1)^J \psi_{rot}$$

rotational parity

$$I\,\psi_{\substack{elec\\ space}} = \pm\,\psi_{\substack{elec\\ space}}$$

as in $\Sigma^{\pm}$ electronic parity

$\infty\sigma_v$ reflection of <u>molecule</u>-fixed <u>electronic</u> coords

$$\infty\sigma_v\,\psi_{\substack{elec\\ space}} = \boxed{\pm}\,\psi_{\substack{elec\\ space}}$$

as in Σ^+ electronic parity

as in Σ^-

same result as

$$I\,\psi_{\substack{elec\\ space}} = \boxed{\pm}\,\psi_{\substack{elec\\ space}}$$

as in $\Sigma^{\pm}$

---

i inversion of <u>molecule</u>-fixed <u>electronic</u> coords

(same as inversion of <u>space</u>-fixed <u>electronic</u> coords)

$$i\,\psi_{\substack{elec\\ space}} = \boxed{\pm}\,\psi_{elec}$$

g

u

as in $\Sigma_g, \Sigma_u \ldots$ $\Pi_g, \Pi_u \ldots$

(ECDMiron)

P_{AB} interchange of nuclei A + B which are indistinguishable

$P_{AB}\,\Psi_{tot} = -\Psi_{tot}$ if I = half integer (FERMIONS)

$P_{AB}\,\Psi_{tot} = +\Psi_{tot}$ if $I = 0$, integer (BOSONS)

$P_{AB}\,\psi_{\substack{nucl\\spin}} = \pm\,\psi_{\substack{nucl\\spin}}$

$+$: ORTHO states

$-$: PARA states

$P_{AB}\,\psi_{rot} = (-1)^J\,\psi_{rot}$

$P_{AB}\,\psi_{elec} = \pm\,\psi_{elec} = (\Sigma^{\pm})(g \text{ or } u)\,\psi_{elec}$

P_{12} interchange of electrons 1 and 2

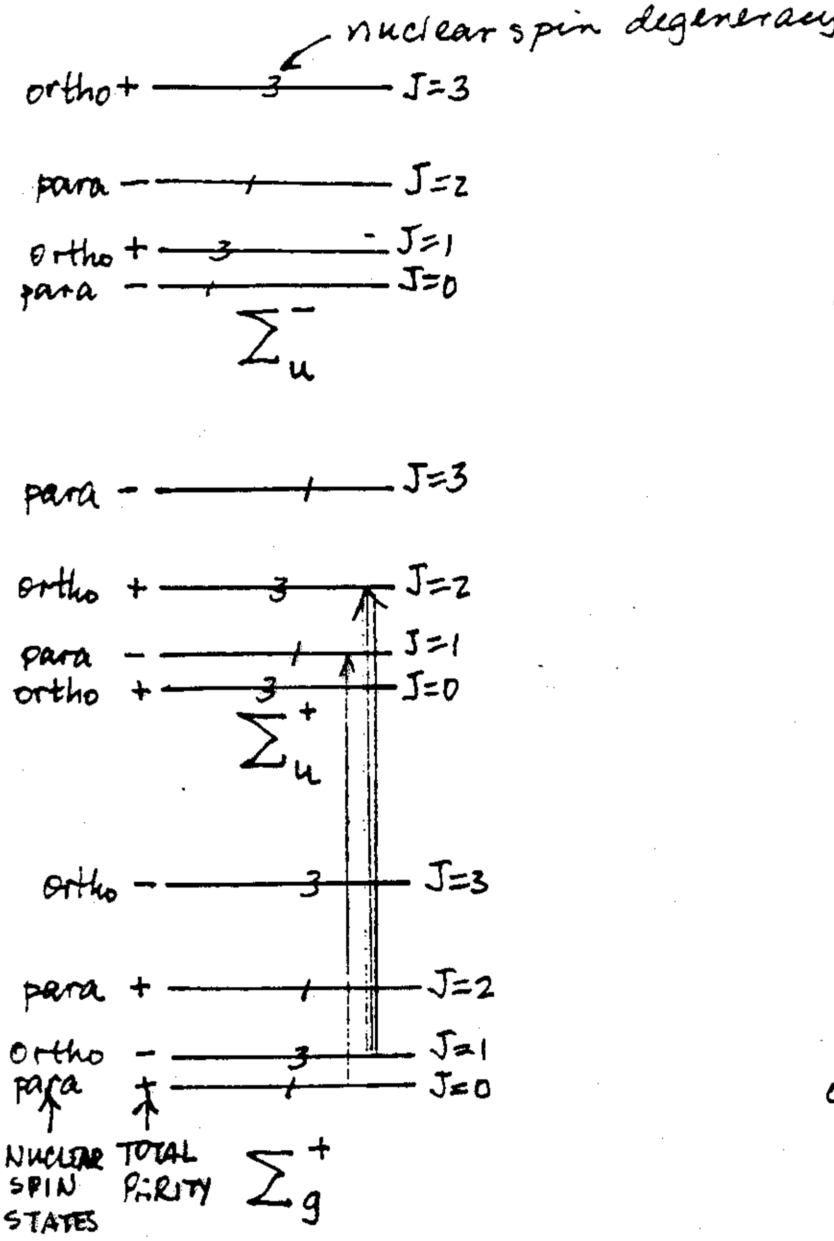
$P_{12}\,\psi_{\substack{elec\\space}}\,\psi_{\substack{elec\\spin}} = -\,\psi_{\substack{elec\\space}}\,\psi_{\substack{elec\\spin}}$

only antisym (electrons are fermions)

$P_{12}\,\psi_{\substack{elec\\spin}} = \pm\,\psi_{\substack{elec\\spin}}$

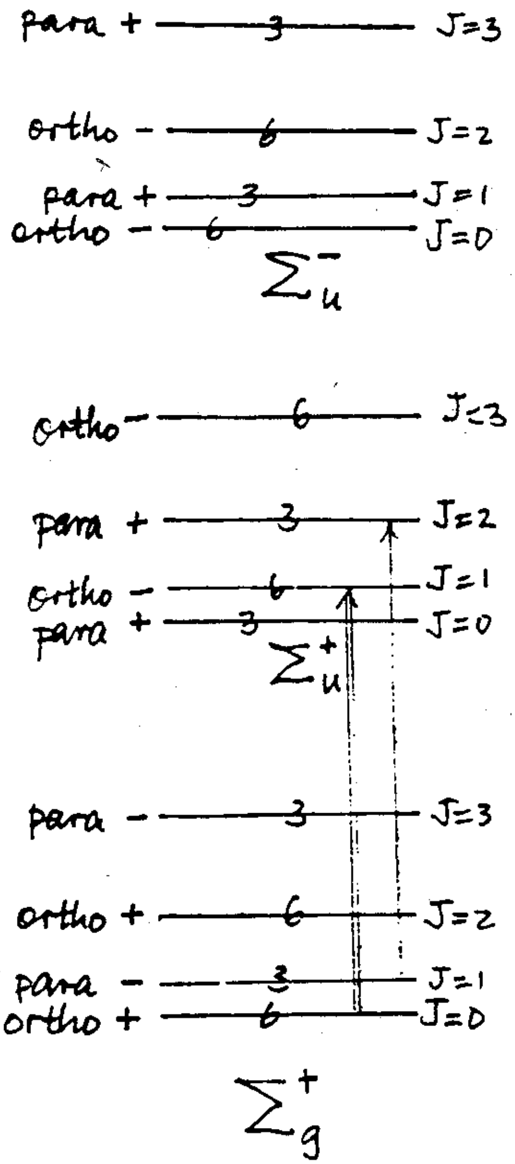
$+$: ORTHO states as in helium

$-$: PARA states



H_2, for example

$I = \frac{1}{2}$ FERMION



D_2, for example

$I = 1$ BOSON

$$P_{AB}\Psi_{tot} = \begin{matrix} +\Psi_{tot} \\ \text{(bosons)} \\ \text{OR} \\ -\Psi_{tot} \\ \underbrace{\text{(fermions)}}_{\text{GIVEN THIS}} \end{matrix} \begin{matrix} = P_{AB}\psi_{elec}^{\Sigma_g^+} \cdot P_{AB}\psi_{rot}^{J} \cdot P_{AB}\psi_{nuclear\ spin} \\ = \underbrace{(+)(g)}_{\text{AND GIVEN THIS}}\psi_{elec}^{\Sigma_g^+} \cdot (-1)^J\psi_{rot}^{J} \cdot (\pm)\psi_{nucl.\ spin} \end{matrix}$$

ONLY ONE SET (ORTHO OR PARA) OF NUCLEAR SPIN STATES CAN GO WITH A PARTICULAR J LEVEL.

H_2, for example

$I = \frac{1}{2}$ FERMION

Nuclear spin states:

$$\text{ORTHO}\begin{cases} \alpha(A)\cdot\alpha(B) \\ \beta(A)\cdot\beta(B) \\ \dfrac{\alpha(A)\beta(B) + \beta(A)\alpha(B)}{\sqrt{2}} \end{cases}$$

$$\text{PARA}\begin{cases} \dfrac{\alpha(A)\beta(B) - \beta(A)\alpha(B)}{\sqrt{2}} \end{cases}$$

D_2, for example

$I = 1$ BOSON

Nuclear spin states:

$$\text{ORTHO}\begin{cases} \alpha(A)\cdot\alpha(B) \\ \beta(A)\cdot\beta(B) \\ \gamma(A)\cdot\gamma(B) \\ \frac{1}{\sqrt{2}}(\alpha(A)\beta(B) + \beta(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\alpha(A)\gamma(B) + \gamma(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\beta(A)\gamma(B) + \gamma(A)\beta(B)) \end{cases}$$

$$\text{PARA}\begin{cases} \frac{1}{\sqrt{2}}(\alpha(A)\beta(B) - \beta(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\alpha(A)\gamma(B) - \gamma(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\beta(A)\gamma(B) - \gamma(A)\beta(B)) \end{cases}$$

In general:

$$\frac{\text{no. of ortho states}}{\text{no. of para states}} = \frac{(I+1)(2I+1)}{I\,(2I+1)}$$