Quartet States in Diatomic Molecules Intermediate Between Cases *a* and *b*

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The determinantal equation given by Hill and Van Vleck for the energies of diatomic molecules intermediate between Hund's cases *a* and *b* has been set up for quartet states and solved by a series method. The solutions are similar in form to those given by Budo for triplet states and the same methods of rotational analysis apply.

THE solutions for the doublet case of Eq. (20) of Hill and Van Vleck[1] are simple and satisfactory for rotational analysis. The triplet case does not yield simple closed formulas, but suitable series solutions have recently been given by Budo[2] and applied successfully to two $^3\Pi$ states of N_2. The purpose of this paper is to develop series solutions for quartet states.

The equation to be solved is

$$\omega^4-\{(10/4)\Lambda^2Y(Y-4)+(9/2)+10J(J+1)\}\omega^2+\{8\Lambda^2Y(Y-1)-4-16J(J+1)\}\omega +(9/16)\Lambda^4Y^2(Y-4)^2+(9/2)\Lambda^2Y(Y-4)J(J+1)+9J^2(J+1)^2-(11/2)J(J+1) -(13/2)\Lambda^2Y-(35/8)\Lambda^2Y^2-(15/16)=0, \quad (1)$$

where σ_k, j and λ of Hill and Van Vleck are replaced by Λ, J and Y and

$$\omega=[W+B\Lambda^2-B\{J(J+1)+5/4\}]/B. \quad (2)$$

If we make

$$y_1=\Lambda^2Y(Y-4)/4, \quad (3)$$

Eq. (1) becomes

$$\omega^4-\{10[y_1+J(J+1)]+9/2\}\omega^2+\{8\Lambda^2Y(Y-1)-4-16J(J+1)\}\omega+9[y_1+J(J+1)]^2 -(11/2)[y_1+J(J+1)]-3\Lambda^2Y^2-12\Lambda^2Y-15/16=0. \quad (4)$$

This is a fourth-order equation of the type,

$$x^4+bx^2+cx+d=0, \quad (5)$$

which has solutions,[3]

$$x=\{-b/2+\tfrac{1}{2}(b^2-4d)^{\frac{1}{2}}\}^{\frac{1}{2}}-c/2(b^2-4d)^{\frac{1}{2}}+\cdots\{-b/2-\tfrac{1}{2}(b^2-4d)^{\frac{1}{2}}\}^{\frac{1}{2}}+c/2(b^2-4d)^{\frac{1}{2}}+\cdots,$$
$$-\{-b/2-\tfrac{1}{2}(b^2-4d)^{\frac{1}{2}}\}^{\frac{1}{2}}+c/2(b^2-4d)^{\frac{1}{2}}+\cdots,\ -\{-b/2+\tfrac{1}{2}(b^2-4d)^{\frac{1}{2}}\}^{\frac{1}{2}}-c/2(b^2-4d)^{\frac{1}{2}}+\cdots. \quad (6)$$

Now $(b^2-4d)^{\frac{1}{2}}=\{64[y_1+J(J+1)]^2+112[y_1+J(J+1)]+49+12\Lambda^2Y^2+48\Lambda^2Y-25\}^{\frac{1}{2}}$

$$=8[y_1+J(J+1)]+7+\{(6\Lambda^2Y^2+24\Lambda^2Y-25/2)/(8[y_1+J(J+1)]+7)\},$$

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[1] Hill and Van Vleck, Phys. Rev. **32**, 261 (1928). See Eq. (20).

[2] Budo, Zeits. f. Physik **96**, 219 (1935).

[3] These solutions may be derived as follows:

Assume that in Eq. (5) $x=\sum_{i=0}^{\infty}x_iy^i$, $b=b_0+b_1y$, $c=c_0+c_1y$, $d=d_0+d_1y$. Substitute these values in Eq. (5) and set the sum of the coefficients of each y^i equal to 0 giving the infinite set of equations,

$$\begin{array}{c} x_0^4+b_0x_0^2+c_0x_0+d_0=0 \\ \{4x_0^3+2b_0x_0+c_0\}x_1+b_1x_0^2+c_1x_1+d_1=0. \\ \vdots \end{array} \quad (I)$$

Set $y=1$ so that $b=b_0+b_1$, $c=c_0+c_1$ and $d=d_0+d_1$. Choose b_0, c_0 and d_0 so that the first of Eqs. (I) can be solved and use further Eqs. (I) to determine x_1, x_2 etc. Specifically make $b_0=b$, $b_1=0$, $c_0=0$, $c_1=c$, $d_0=d$ and $d_1=0$ which reduces the first of Eqs. (I) to a quadratic in x_0^2. The solutions given by Budo for the triplet case may be derived in a similar manner.

neglecting higher terms in the expansion. If we set[4]

$$\delta=\{6\Lambda^2Y^2+24\Lambda^2Y-25/2\}/\{8[y_1+J(J+1)]+7\},$$

$$(b^2-4d)^{\frac{1}{2}}=8[y_1+J(J+1)]+7+\delta.$$

Solutions (6) become,

$$\begin{aligned}
\omega_4&=\left\{9[y_1+J(J+1)]+\frac{23}{4}+\frac{\delta}{2}\right\}^{\frac{1}{2}}-\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}+\cdots,\\
\omega_3&=\left\{y_1+J(J+1)-\frac{5}{4}-\frac{\delta}{2}\right\}^{\frac{1}{2}}+\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}+\cdots,\\
\omega_2&=-\left\{y_1+J(J+1)-\frac{5}{4}-\frac{\delta}{2}\right\}^{\frac{1}{2}}+\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}+\cdots,\\
\omega_1&=-\left\{9[y_1+J(J+1)]+\frac{23}{4}+\frac{\delta}{2}\right\}^{\frac{1}{2}}-\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}+\cdots.
\end{aligned}\tag{7}$$

Neglecting the constant, $-B\Lambda^2+B5/4$, in the energy and terms beyond the second in ω,

$$\begin{aligned}
W=F_4(J)&=B\left[J(J+1)+\{9y_1+9J(J+1)+23/4+\delta/2\}^{\frac{1}{2}}-\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}\right],\\
F_3(J)&=B\left[J(J+1)+\{y_1+J(J+1)-5/4-\delta/2\}^{\frac{1}{2}}+\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}\right],\\
F_2(J)&=B\left[J(J+1)-\{y_1+J(J+1)-5/4-\delta/2\}^{\frac{1}{2}}+\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}\right],\\
F_1(J)&=B\left[J(J+1)-\{9y_1+9J(J+1)+23/4+\delta/2\}^{\frac{1}{2}}-\frac{\Lambda^2Y(Y-1)-\frac{1}{2}-2J(J+1)}{2y_1+7/4+\delta/4+2J(J+1)}\right].
\end{aligned}\tag{8}$$

When J becomes large the solutions approach the values, $B(J^2+4J+10/4)$, $B(J^2+2J-2/4)$, $B(J^2-6/4)$ and $B(J^2-2J-2/4)$, i.e., if we add the term $+(5/4)B$ which was dropped from the energies, they approach the values, $BK(K+1)$, where $K=(J+3/2)$, $(J+\frac{1}{2})$, $(J-\frac{1}{2})$ and $(J-3/2)$, respectively.

The second differences are

$$\begin{aligned}
\Delta_2F_4(J)&=4B(J+\tfrac{1}{2})\Bigg[1+9/2\{9y_1+23/4+\delta/2+9J(J+1)\}^{-\frac{1}{2}}\\
&\qquad+\frac{3\Lambda^2Y^2-6\Lambda^2Y+5/2+\delta/2}{\{2y_1+7/4+\delta/4+2(J+1)(J+2)\}\{2y_1+7/4+\delta/4+2(J-1)J\}}\Bigg],\\
\Delta_2F_3(J)&=4B(J+\tfrac{1}{2})\Bigg[1+\tfrac{1}{2}\{y_1-5/4-\delta/2+J(J+1)\}^{-\frac{1}{2}}\\
&\qquad-\frac{3\Lambda^2Y^2-6\Lambda^2Y+5/2+\delta/2}{\{2y_1+7/4+\delta/4+2(J+1)(J+2)\}\{2y_1+7/4+\delta/4+2(J-1)J\}}\Bigg],
\end{aligned}\tag{9}$$

[4] This term is carried as δ since it may have an appreciable value for small J. It can easily be computed from the value of Y determined by first approximation.

$$\Delta_2F_2(J)=4B(J+\tfrac{1}{2})\left[1-\tfrac{1}{2}\{y_1-5/4-\delta/2+J(J+1)\}^{-\frac{1}{2}}\right.$$

$$\left.-\frac{3\Lambda^2Y^2-6\Lambda^2Y+5/2+\delta/2}{\{2y_1+7/4+\delta/4+2(J+1)(J+2)\}\{2y_1+7/4+\delta/4+2(J-1)J\}}\right],$$

$$\Delta_2F_1(J)=4B(J+\tfrac{1}{2})\left[1-9/2\{9y_1+23/4+\delta/2+9J(J+1)\}^{-\frac{1}{2}}\right.$$

$$\left.+\frac{3\Lambda^2Y^2-6\Lambda^2Y+5/2+\delta/2}{\{2y_1+7/4+\delta/4+2(J+1)(J+2)\}\{2y_1+7/4+\delta/4+2(J-1)J\}}\right],$$

when $\{C+(J+1)(J+2)\}^{\frac{1}{2}}+\{C+(J-1)J\}^{\frac{1}{2}}$ is set $=2\{C+J(J+1)\}^{\frac{1}{2}}$. ($C=9y_1+23/4+\delta/2$ or $y_1-5/4-\delta/2$). In determining the constant, B, the mean of the $\Delta_2Fs=4B(J+\frac{1}{2})$ should be used. This may be seen from Eqs. (9) or more rigorously from the fact that the sum of solutions for $\omega=0$ for all values of J since the coefficient of the cubic term $=0$ in Eq. (4). It is probably necessary to add a term $DK^2(K+1)^2$ to Eqs. (8) and $8D(K+\frac{1}{2})^3$ to Eqs. (9) in order to get well fitting curves. This point and other details of analysis are ably discussed by Budo.

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