Uniform WKB 파동함수와 Franck-Condon 인수*

趙 雄 仁 · 兪 炳 贊**

카나다 McGill 대학교 화학과

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Uniform WKB Wavefunctions and Franck-Condon Factors*

Ung-In Cho and Byung Chan Eu**

Department of Chemistry, McGill University, Montreal, Canada

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요 약. 2-전향점 문제의 Uniform WKB 파동함수의 정밀도를 대응하는 수치해와 비교하고 검토한 결과 Uniform WKB 파동함수가 대단히 정밀하다는것을 발견하였다. 그러한 파동함수의 응용의 예로서 model 계에 대한 Franck-Condon 인자들을 계산하였으며 계산된 인자들의 정밀도도 역시 매우 높다는것을 보였다. Uniform WKB 파동함수를 이용하여 Franck-Condon 인자의 점근치를 검토하였으며 전환진동수에 대한 Mulliken 의 조건, $E'_{n'J'}-U'_{eff}(r_s)=E''_{n''J''}-U''_{eff}(r_s)$, 을 유도하였다.

Abstract. The accuracy of the uniform WKB solution for a two-turning point problem is examined in comparison with the corresponding numerical solution. It is found that the uniform WKB solution is extremely accurate. Various Franck-Condon factors for a model system are calculated as an example of applications of such approximate wavefunction. The accuracy of the factors thus calculated is very good. By using the uniform WKB wavefunctions, we have examined the asymptotic limit of the Frank-Condon factors and derived the condition for the frequencies of the transitions, $E'_{n'J'}-U'_{eff}(r_s)=E''_{n''J''}-U'_{eff}(r_s)$, which was obtained by Mulliken using physical arguments.

1. Introduction

Many approximate interpretations of molecular transitions through the molecular interactions with electron, photon, and another molecule may be achieved in terms of the Franck-Condon factors for the transitions. Therefore, calculation of Franck-Condon factors[1] is of a considerable interest and importance to many research workers. At present, the exact calculation of Franck-Condon factors does not pose a problem except for the laborious process required of calculating various vibration-rotation wavefunctions of diatomic molecules. Nevertheless, it is useful to have an approximate yet sufficiently accurate method of calculating them. One of

two aims of this paper is to report on such a calculation with the uniform WKB wavefunctions for bound state(two-turning point) problems, which turned out to be extremely accurate. Recently, Mulliken[2] discussed the role of the kinetic energy in Franck–Condon transitions and discovered that the frequency of radiation accompanying the transitions should in general depend on the position *via* a relation

$$E'' = E' - U'_{eff}(r) + U''_{eff}(r), \qquad (1.1)$$

which we call Mulliken's condition. He arrived at this condition through physical arguments. The other aim of this paper is to derive (1.1) by using the semiclassical wavefunction. The condition we obtain is more general than Mulliken's, leading to his condition after approximation.

In Section 2 we present the uniform WKB wavefunctions for arbitrary vibrational and rotational states. In Section 3 we discuss the accuracy of such wavefunctions by comparing them with the corresponding numerical wavefunctions. We also present the Franck–Condon factors calculated for $A_2 \rightarrow A_2^+$ transitions where A_2 and A_2^+ are a model diatormic molecule and its ion. In Section 4 we discuss an asymptotic evaluation of Franck–Condon factors and derive Mulliken's condition in the limit of large vibrational quantum numbers.

2. Uniform WKB Wavefunction

The solution of a Schroedinger equation can be expressed in terms of two independent solutions of the second order differential equation and the coefficients of the expansion(integration constants) can be suitably fixed by imposing appropriate boundary conditions. The WKB method of solution provides a very general technique of solving such an equation in approximation and rather accurate eiqenvalues

which can be calculated from the classical quantization condition,

$$\hbar^{-1} \int_{r_1}^{r_2} [2m(E_n - U_{eff})]^{\frac{1}{2}} dr = \left(n + \frac{1}{2} \right) \pi, \quad (2.1)$$

where n is an integer(e. g., vibrational quantum number) ranging from 0 to a certain value, U_{eff} an effective potential, m the reduced mass, r_1 and r_2 the classical turning points. The eigenvalues obtained from(2.1) agree rather well with those obtained by the numerical solution method[2] except for the uppermost vibrational states. However, the usual WKB wavefunctions are poor in accuracy and specially so around the classical turing points where the WKB solutions break down completely.

Miller and Good[4], Langer[5], and Kazarinoff[6] investigated a uniformization of the WKB solutions. The uniformized(uniform) WKB solutions are valid over the entire domain of variable and we find them very accurate and almost comparable to the numberical wavefunctions.

Since it is necessary to define the notations involved, we might as well make this article self-contained by describing how the uniform WKB solution is obtained.

Let the radial Schroedinger equation be

$$\left[-\frac{d'^2}{dr^2} + \lambda^2 (E - U_{eff}) \right] u(r) = 0, \qquad (2.2)$$

where the effective potential is given by

$$U_{eff} = U(r) + J(J+1)/\lambda^2 r^2, \quad (\lambda^2 = 2m/\hbar^2), \qquad (2.3)$$

$U(r)$ being a potential function. It is convenient to define

$$p(r) = [E - U_{eff}(r)]^{\frac{1}{2}}. \qquad (2.4)$$

Now introduce a new variable s such that

$$\int_{-c}^{s} (c^2 - t^2)^{\frac{1}{2}} dt = \int_{r_1}^{r} dr' p(r'), \qquad (2.5)$$

where c is a positive constant yet to be determined. The two turning points are defined by

$$p^2(r_i) = 0 \qquad (i=1, 2)$$

and

$$r_2 > r_1.$$

With definition of $z = s/c$, we may write (2.5) in the form,

$$c^2 \int_{-1}^{z} (1-t^2)^{\frac{1}{2}} dt = \int_{r_i}^{r} dr' p(r'). \qquad (2.5a)$$

Since we can equally well define the variable s (or z) in reference to the outer turning point r_2 instead of the inner one r_1 as follows,

$$c^2 \int_{z}^{1} (1-t^2)^{\frac{1}{2}} dt = \int_{r}^{r_2} dr' p(r'), \qquad (2.5b)$$

we demand the following "normalization condition",

$$c^2 \int_{-1}^{1} (1-t^2)^{\frac{1}{2}} dt = \int_{r_1}^{r_2} dr\, p(r) = \frac{1}{2}\pi c^2. \qquad (2.6)$$

That is, the constant c is defined such that

$$c^2 = (2/\pi) \int_{r_1}^{r_2} dr\, p(r). \qquad (2.7)$$

The transformation (2.5) of r to s is one to one and we can regard r as a monotonic function of s,

$$s = r(s).$$

Introduce a transformation

$$u(r) = (dr/ds)^{\frac{1}{2}} y(s). \qquad (2.8)$$

Then $y(s)$ satisfies the differential equation,

$$\left[\frac{d^2}{ds^2} + \lambda^2(c^2 - s^2) \right] y(s) = -\frac{1}{2} \{r, s\} y(s), \qquad (2.9)$$

where the Schwartzian derivative $\{r, s\}$ is defind by

$$\{r, s\} = (r''/r') - (3/2)(r''/r')^2, \qquad (2.10)$$
$$r' = dr/ds, \text{ etc.}$$

The λ is a large parameter in the equations (2.2) and (2.9) which may serve as an expan-

sion parameter for an asymptotic series solution of (2.9). Since the Schwartzian derivative is $0(\lambda^0) = 0(1)$ in the limit $\lambda \to \infty$, i.e., the classical limit, we can neglect the rhs of (2.9) in comparison with the second term on the lhs, which is $0(\lambda^2)$. This is in accordance with the spirit of the WKB method of solution. We may thus define the lowest order solution $y^{(0)}(s)$ of (2.9) by the differential equation,

$$\left[\frac{d^2}{ds^2} + \lambda^2(c^2 - s^2) \right] y^{(0)}(s) = 0. \qquad (2.11)$$

In other words, $y^{(0)}(s)$ is the leading term of the asymptotic expansion of $y(s)$. Equation (2.11) is exactly in the same form as the Schroedinger equation for a simple harmonic oscillator. Thus, it can be solved by the usual procedure and we only list the important results.

If there exists a positive integer n such that

$$\lambda c^2 = 2n + 1, \qquad (2.12)$$

then the solution of (2.11) satisfying the boundary condition is

$$y_n^{(0)}(\xi) = N_n \exp\left(-\frac{1}{2}\xi^2\right) H_n(\xi), \qquad (2.13)$$

where

$$\xi = \sqrt{\lambda}\, s = \sqrt{\lambda}\, cz, \qquad (2.14)$$

and the normalization constant N_n is given by the expression

$$N_n^{-2} = \int_0^\infty dr(dr/ds) \exp(-\xi^2) H_n^2(\xi). \qquad (2.15)$$

The function $H_n(\xi)$ is the Hermite polynomial of order n. A remarkable thing about the approximate wavefunction is that except for the factor $(dr/ds)^{\frac{1}{2}}$, it is exactly in the same form as that for a simple harmonic oscillator. However, the similarity ends there in their forms only, since the arguments are different.

Now we examine the meaning of (2.12). On substitution of (2.7) into (2.12), we obtain

$$\lambda \int_{r_1}^{r_2} dr\ p(r) = \left(n + \frac{1}{2}\right)\pi, \qquad (2.16)$$

which is precisely the formula for the WKB eigenvalues, i.e., (2.1). This equation supplies the interpretation of n that it is the vibrational quantum number of the bound state. This in turn means that the wavefunction $u_n^{(0)}(r)$ has precisely n nodes.

In order to understand better the behaviour of the wavefunction, we schematically plot z as a function of r in *Fig.* 1. The curve maintains its shape generally for any potential with a repulsive and attractive branches as shown in *Fig.* 1. We see from *Fig.* 1 that

$$-\infty < z < -1 \text{ for } 0 \leqslant r < r_1, \quad (a)$$
$$-1 \leqslant z \leqslant 1 \quad \text{for } r_1 \leqslant r \leqslant r_2, \quad (b) \quad (2.17)$$
$$1 < z < \infty \quad \text{for } r_2 < r < \infty. \quad (c)$$

Since $H_n(-\xi) = (-1)^n H_n(\xi)$ and
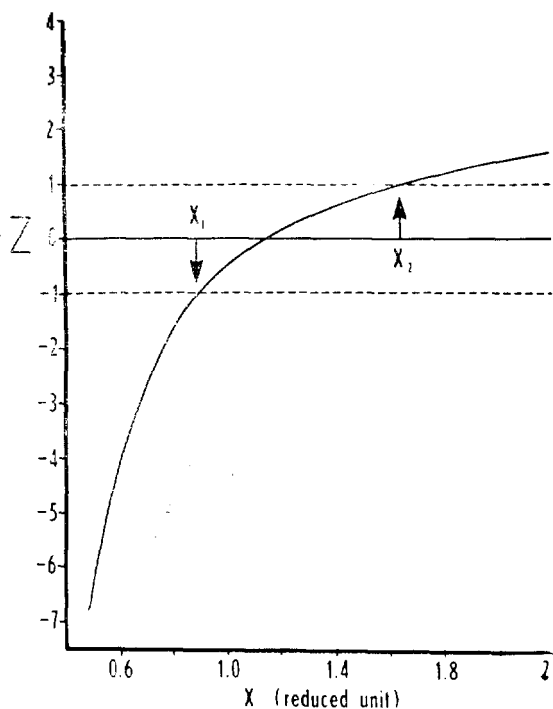
$$H_n(\xi) \xrightarrow[\xi \to \infty]{} \xi^n,$$

X (reduced unit)

Fig. 1. A Schematic plot of z vs. r

we see that

$$y_n^{(0)}(\xi) \xrightarrow[\xi \to \pm\infty]{} N_n(\pm\xi)^n \exp\left(-\frac{1}{2}\xi^2\right),$$

$$(|\xi| \gg \sqrt{\lambda}\ c). \qquad (2.18)$$

That is, $y_n^{(0)}(\xi)$ is an exponentially decreasing function of ξ if $|\xi| > \sqrt{\lambda}\ c$. In the region $-1 \leqslant z \leqslant 1$ the function $H_n(\xi)$ is an oscillating function.

It is convenient for our discussion in Section 4 to list some of the asymptotic formulas[7] for $H_n(\xi)$ in the region $[-1, 1]$ of z: The Hermite polynomial can be given in terms of the Airy function $A_i(-t)$,

$$\exp\left(-\frac{1}{2}Nz^2\right)H_n(\sqrt{N}\ z) = (2\pi)^{\frac{1}{2}}N^{\frac{1}{2}(n+\frac{1}{3})} \cdot$$

$$\exp\left(-\frac{1}{4}N\right)|\ \phi'\ |^{-\frac{1}{4}}\ A_i\left(-N^{\frac{2}{3}}\phi\right)\left[1+0\left(\frac{1}{n}\right)\right],$$

$$(N = 2n+1) \qquad (2.19)$$

where

$$\frac{2}{3}\phi^{\frac{3}{2}} \equiv -\frac{1}{2}z(1-z^2)^{\frac{1}{2}} + \frac{1}{2}\cos^{-1}z$$

$$= c^{-2}\int_{r_1}^{r} dr'\ p(r'), \quad (-1 \leqslant z \leqslant 1), \qquad (2.20a)$$

$$\frac{2}{3}(-\phi)^{\frac{3}{2}} \equiv \frac{1}{2}z(z^2-1)^{\frac{1}{2}} - \frac{1}{2}\log|z +$$

$$(z^2-1)^{\frac{1}{2}}| = \begin{cases} c^{-2}\int_{r_2}^{r} dr'\ p(r'), & (z > 1), \\ c^{-2}\int_{r}^{r_1} dr'\ p(r'), & (z < -1). \end{cases}$$

$$(2.20b)$$

It is useful to note that

$$\frac{ds}{dr} = \frac{p(r)}{(c^2-s^2)^{1/2}} \sim c^{-1}E_{nJ}^{1/2}, \qquad (2.21)$$

if

$$E_{nJ} > U_{\text{eff}}.$$

It is also useful for the discussion in Section 4 to list the expression[8] for the Airy function $A_i(-t)$,

$$A_i(-t) = M(t)\cos\theta(t) \qquad (2.22)$$

where

$$M(t) = [A_i^2(-t) + B_i^2(-t)]^{1/2},$$

and

$$\theta(t) = \tan^{-1}[B_i(-t)/A_i(-t)].$$

$B_i(-t)$ is defined as in Ref. 8, p. 449.

In the next sections we shall examine the numerical accuracy of the wavefunctions $u_n^{(0)}$ as given by (2.15), also calculate the Franck-Condon factors as an example for the utility of the wavefunctions. We shall also study the Franck-Condon factors in relation to Mulliken's condition.

3. Numerical Accuracy of $u_n^{(0)}$ and Semiclassical Franck-Condon Factors

In this section, we shall show the accuracy of the wavefunction $u_n^{(0)}$ obtained in the previous section and then use it for semiclassical calculations of Franck-Condon factors.

In order to carry out calculations, it is necessary to choose a system and the corresponding potential functions. We choose model potentials which are linear combinations of exponential functions,

$$U(r) = D_e \sum_{j=1}^{n} a_j \exp(-\alpha j x),$$

$$x = r - r_{eq}. \tag{3.1}$$

This function qualitatively reproduces the known potentials of the $H_2 - H_2^+$ system[9,10]. Since our first objective here is in comparison of the wavefunctions in the numerical and uniform WKB methods, we use the model potentials. This allows us to avoid laborious process of fitting analytic forms to the numerical potentials to a high accuracy. We emphasize that this, however, does not diminish the value of the comparison we are making below. The varios parameters in (3.1) are defined by

$$D_e = 0.17447 \text{ au}$$

$$\alpha = 0.500 \text{ au}$$
$$r_{eq} = 1.401 \text{ au}$$

for the initial state (A_2) and

$$D_e = 0.10263 \text{ au}$$
$$\alpha = 0.325 \text{ au}$$
$$r_{eq} = 2.00 \text{ au}$$

for the final state (A_2^+). The expansion parameters are listed in *Table* 1.

With the potentials thus defined, we have calculated the uniform WKB wavefunctions for various vibrational-rotational states and compared them with the corresponding wavefunctions obtained by solving the radial Schroedinger equation (2.2) in a numerical method. We have used the standard Runge-Kutta-Gill method of solution for the numerical wavefunctions[3].

In calculating $u_n^{(0)}$, we have used a lower order Gaussian quadrature for the calculation of the phase integrals appearing in (2.5) and then a recurrence relation to compute the Hermite polynomials. We have checked the reliability of the wave functions thus calculated against those with different integration step sizes for the calculation of the phase integral and also with different integration routines. The wavefunctions are found reliable to the sixth place below the decimal point for most of the cases considered. The accuracy of the numerical wavefunctions is achieved approximately to the order of 10^{-6}.

In *Table* 2 we compare the WKB and numerical eigenvalues of A_2 and A_2^+ in order to show the reliability of the WKB method. The vibrational eigenvalues are generally quite reliable except for the states near the dissociation limit. In *Table* 3, listed are some sample values of the uniform WKB and numerical wavefunctions for vibrational-rotational state $n=6$ and $J=4$. The uniform WKB wavefunctions are surprisingly accurate in comparison with the numerical

Table 1. Potential parameters a_i

	A_2	A_2^+
a_1	-0.00004	-0.059
a_2	-0.204	1.331
a_3	0.928	-27.213
a_4	-51.798	121.620
a_5	204.620	-327.821
a_6	-393,443	555,034
a_7	455.804	-581.700
a_8	-335.274	365.281
a_9	154,546	125.762
a_{10}	-40.984	18.290
a_{11}	4.805	—

Table 2. Eigenvalues, the WKB and numerical (in the units of D_r)

		WKB		Numerical	
n	J	A_2	A_2^+	A_2	A_2^+
0	0	-0.9433	-0.9480	-0.9430	-0.9477
2	0	-0.7322	-0.7610	-0.7318	-0.7606
4	0	-0.5452	-0.5949	-0.5447	-0.5945
6	0	-0.3818	-0.4481	-0.3812	-0.4475
10	0	-0.1299	-0.2139	-0.1293	-0.2133
16	0	—	-0.0197	—	-0.0192
0	4	-0.9127	-0.9222	-0.9125	-0.9219
2	4	-0.9047	-0.7382	-0.7043	-0.7378
4	4	-0.5206	-0.5745	-0.5201	-0.5741
6	4	-0.3602	-0.4301	-0.3596	-0.4295
10	4	-0.1150	-0.2006	-0.1144	-0.2000
16	4	—	-0.0145	—	-0.0141

wavefunction for the same state. In view of the fact that it is quite laborious to obtain accurate wavefunctions numerically, the uniform WKB solution with such an accuracy should be very useful for various calculations involved in studies of many molecular processes. [11]

For an application of $u_n^{(0)}$ thus calculated we have calculated the Franck–Condon Factors for the transitions $A_2 \rightarrow A_2^+ + e$, where A_2 is a model molecule in the initial state and A_2^+ the

Table 3. Wavefunctions, the uniform WKB and numerical ($n=6$, $J=4$)

r	Uniform WKB		Numerical	
	A_2	A_2^+	A_2	A_2^+
1	1.012240	0.032845	1.014635	0.032947
1.14	0.026278	0.194502	0.026291	0.195076
1.26	-0.879645	0.544837	-0.881714	0.546270
1.37	-0.050981	0.930532	-0.051269	0.932553
1.49	0.869426	0.965951	0.871463	0.967250
1.60	0.001315	0.333606	0.001822	0.333027
1.72	-0.893920	-0.632504	-0.895984	-0.634486
1.84	0.017132	-0.834909	0.016241	-0.835998
1.97	0.946797	0.104297	0.948907	0.105388
2.11	-0.041903	0.893738	-0.040584	0.895369
2.26	-1.048373	0.096929	-1.050467	0.096768
2.44	0.028539	-0.918267	0.026932	-0.919877
2.70	1.370443	0.741323	1.371307	0.742190
3.70	0.004264	1.334132	0.004357	1.334703
3.90	0.000714	1.275815	0.000731	1.272431

ion in the final state. The Franck–Condon factor is given by the expression,

$$Q(n'J';n''J'') = |\int_0^\infty dr\, u'(n'J',r)u'' \cdot (n''J'',r)|^2, \quad (3.2)$$

where $u'(n'j',r)$ and $u''(n''j'',r)$ are the vibrational-rotational wavefunctions of the initial and final states, respectively. In the semiclassical approximation, we have

$$Q^{(0)}(n'j';n''J'') = |\int_0^\infty dr\, u^{(0)'}(n'J',r) \cdot u^{(0)''}(n''J'',r)|^2, \quad (3.3)$$

where $u^{(0)}$ are the uniform WKB wavefunctions. In Fig. 2a we have plotted the wavefunctions, the uniform WKB and numerical, along the corresponding probability amplitudes, $P(n'J'; n''J'') = u'(n'J')\, u''(n''J'')$ and $P^{(0)} = u^{(0)'}(n'J')u^{(0)''}(n''J'')$. In Fig. 2~3 we have plotted the wavefunctions $u^{(0)'}(n''J'')$ along with $P^{(0)}$ in order to show the behaviours of the proba-
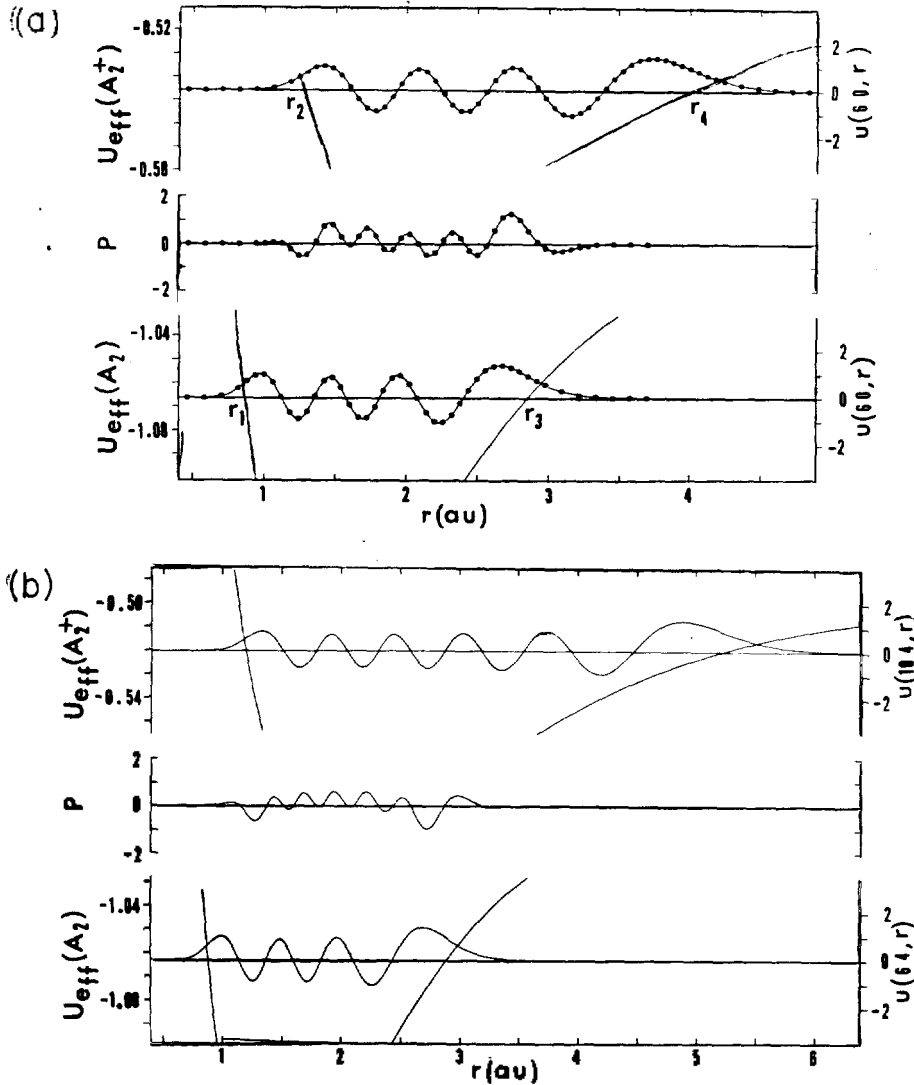
Fig. 2*a.* The uniform WKB and numerical wavefunctions and the probability amplitudes plotted against the distance. The solid curve represents the uniform WKB results and the solid circles the numerical result. r_1, r_2, r_3, and r_4 are the classical turning points.

2*b.* The uniform WKB wavefunctions and the probability amplitude plotted against the distance. The initial state is $(n, J) = (6, 4)$ and the final state $(10, 4)$.

bility amplitudes and the reliability of the uniform WKB wavefunctions for different n and J. Since the numerical wavefunctions are graphically almost indist inguishable from $u^{(o)}$, we have indicated the numerical wavefunctions with filled circles in *Fig.* 2*a* only.

The Franck–Condon factors are computed numerically by integrating (3.2) and (3.3), respectively. We have used a Simpson's rule for the integration. In *Table* 4 we list some of Franck–Condon factors thus calculated. We see that the semiclassical Franck–Condon factors
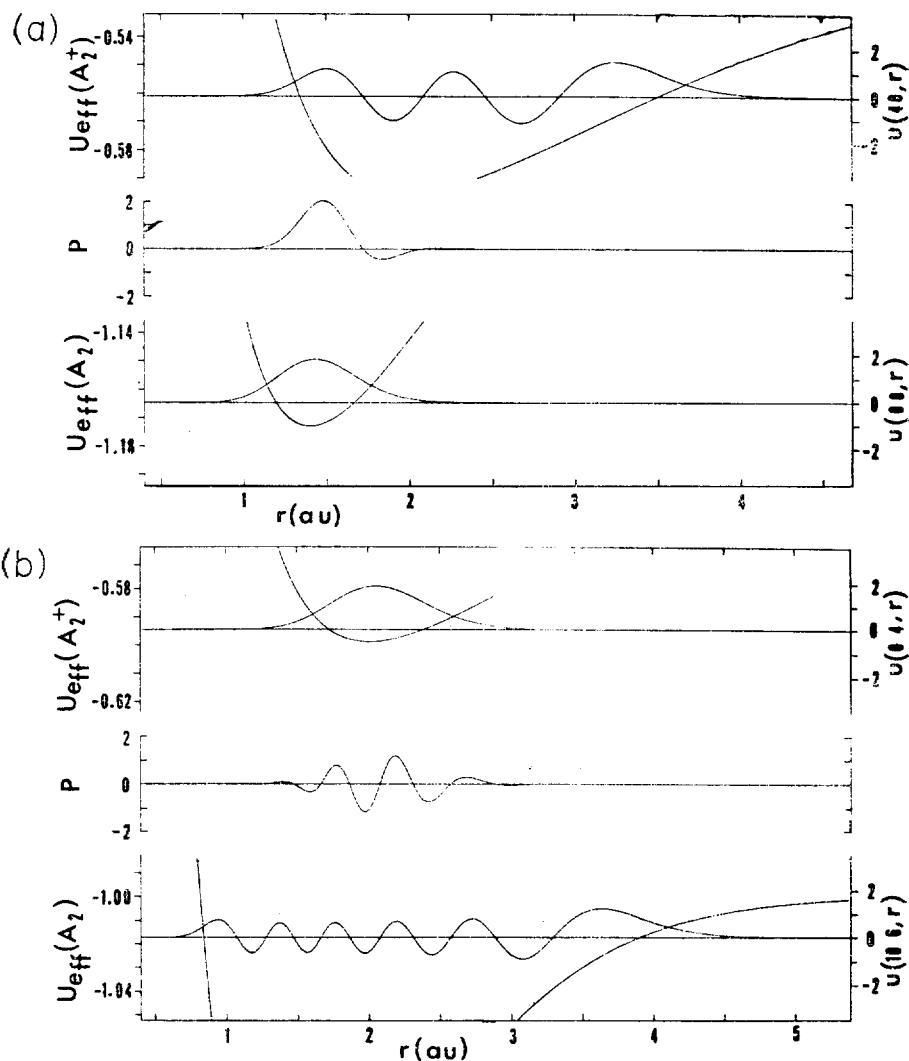
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Fig. 3*a*. The uniform WKB wavefunctions and the probability amplitude for the transition (0.0)→(4,0).

    3*b*. The uniform WKB wavefunction and the probability amplitude for the transition (10,6)→(0,4). Unlike in the case for *Fig*, 3*a*. the Franck–Condon factor is expected to be rather small due to the symmetric behaviour of *P* around the *axis* along *r*.

are quite comparable with the numerical ones.

The utility of the uniform WKB wavefunction presented here is not confined only to calculations of the Franck–Condon factors, but also obviously includes various calculations in molecular collision processes[11].

4. The Asymptotic Evaluation of $Q^{(o)}$

Recently, Mulliken[2] has discussed the *r*-dependence of the frequencies corresponding to the Franck–Condon transitions in the limit of high vibrational states. In fact, he has obtained

Table 4. Franck-Condon fators $[A_2(J,n)\to A_2^+(J',n')+e]$

n' \ n	0 a	0 b	2 a	2 b	4 a	4 b	6 a	6 b	10 a	10 b
0	0.0979 (0.0984)c	0.1177 (0.1182)	0.3361 (0.3355)	0.3323 (0.3307)	0.0659 (0.0649)	0.0520 (0.0510)	0.0010 (0.0010)	0.0005 (0.0005)	0.0 (0.0)	0.0 (0.0)
2	0.1710 (0.1713)	0.1820 (0.1823)	0.0744 (0.0744)	0.1011 (0.1009)	0.0028 (0.0029)	0.0193 (0.0191)	0.2748 (0.2735)	0.2538 (0.2520)	0.0 (0.0)	0.0 (0.0)
4	0.1163 (0.1166)	9.1117 (0.1119)	0.0648 (0.0650)	0.0494 (0.0497)	0.0687 (0.0687)	0.0463 (0.0470)	0.1096 (0.1093)	0.0820 (0.0816)	0.0287 (0.0275)	0.0070 (0.0066)
6	0.0612 (0.0614)	0.0538 (0.0540)	0.0013 (0.0013)	0.0003 (0.0003)	0.0074 (0.0073)	0.0219 (0.0217)	0.0307 (0.0306)	0.0548 (0.0547)	9.2612 (0.2623)	0.4112 (0.4113)
10	0.0144 (0.0145)	0.0111 (0.0112)	0.0232 (0.0235)	0.0299 (0.0306)	0.0258 (0.0263)	0.0180 (0.0186)	0.0012 (0.0012)	0.0006 (0.0007)	0.0352 (0.0365)	0.0197 (0.0202)
16	0.0016 (0.0016)	0.0011 (0.0011)	0.0105 (0.0105)	0.0096 (0.0097)	0.0 (0.0)	0.0002 (0.0002)	0.0073 (0.0074)	0.0077 (0.0078)	0.0042 (0.0043)	0.0065 (0.0065)

a : $A_2(O,n)\to A_2^+(O,n')+e$,   b : $A_2(6,n)\to A_2^+(4,n')+e$,   c : Numbers in parenthesis are numerical calculation

the condition (1.1) from which one can calculate the r-dependence of the frequency of a transition. He arrived at the condition through physical arguments. In this section, we shall derive the condition (1.1) by investigating the asymptotic behaviour of $Q^{(0)}$ as n' and n'' increase to a large number. Therefore, the present derivation will provide a mathematical basis for Mulliken's condition. In fact, we obtain a more general condition that reduces to (1.1) on an approximation.

For this purpose, let us consider the integral

$$q(n'J';n''J'') \equiv \int_0^\infty dr\; u^{(0)'}(n'J',r) \cdot$$
$$u^{(0)''}(n''J'',r). \tag{4.1}$$

We arrange the four classical turning points corresponding to the energies $E_{n'J'}$ and $E_{n''J''}$ in an increasing sequence.

$$r_1 < r_2 < r_3 < r_4.$$

The subsequent discussion will be valid regardless of which turning points correspond to which states, but it is convenient to assign them to specific potential curves. We will assume, without loss of generality, that r_1 and r_3 correspond to the potential curve of the initial state and r_2 and r_4 to that of the final state (see

Fig. 2). We must consider the following cases separately: (1) the case in which $D_{12} \equiv r_2 - r_1$ and $D_{34} \equiv r_4 - r_3$ are sufficiently large so that there are a large number of oscillation in the interval; (2) the case in which $D_{12}/D_{13} \ll 1$ and $D_{34}/D_{24} \ll 1$, where D_{13} and D_{34} are defined similarly to D_{12} and $D_{34'}$ so that we may set $r_1 \approx r_2$ and $r_3 \approx r_4$ to a good approximation.

With the turning points thus arranged, we can rewrite (4.1) in the following forms: for the case 1

$$q = \left(\int_0^{r_1} + \int_{r_1}^{r_2} + \int_{r_2}^{r_3} + \int_{r_3}^{r_4} + \int_{r_4}^\infty\right) dr\; u^{(0)'}(n'J',r) \cdot$$
$$u^{(0)}(n''J'',r), \tag{4.2a}$$

and for the cnse 2

$$q = \left(\int_0^{r_1} + \int_{r_2}^{r_3} + \int_{r_3}^\infty\right) dr\; u^{(0)'}(n'J',r) \cdot$$
$$u^{(0)''}(n''J'',r). \tag{4.2b}$$

In the classically forbidden regions $[0, r_1]$ and $[r_4, \infty]$ both wavefunctions are very small exponentially decreasing functions and thus we may neglect the integrals over such regions. Then, we obtain in approximation

$$q \approx q_1 + q_2 + q_3, \tag{4.3a}$$

and

$$q \approx q_2 \tag{4.3b}$$

where

$$q_1 = \int_{r_1}^{r_2} dr\, u^{(0)\prime}(n'J', r)u^{(0)\prime\prime}(n''J'', r), \quad (4.4)$$

$$q_2 = \int_{r_2}^{r_3} dr\, u^{(0)\prime}(n'J', r)u^{(0)\prime\prime}(n''J'', r), \quad (4.5)$$

$$q_3 = \int_{r_3}^{r} dr\, u^{(0)\prime}(n'J', r)u^{(0)\prime\prime}(n''J'', r). \quad (4.6)$$

In (4.5) both wavefunctions are oscillatory if the vibrational quantum number is not equal to 0, while in (4.4) and (4.6) only one wavefunction is oscillatory, the other one being an exponentially decreasing function.

Since in the limit of large n' and n'' the oscillating part of the wavefunctions may be written in the form of (2.19) in terms of A_i $(-t)$, when (2.22) is used, the intergrals (4.4 ∼6) may be given in the form,

$$q_1(\infty) = \int_{r_1}^{r_2} dr\, A'(r)\bar{A}''(r)A_i(t'')\cos\theta'(r), \quad (4.7)$$

$$q_2(\infty) = \int_{r_2}^{r_3} dr\, A'(r)A''(r)\cos\theta'(r)\cos\theta''(r), \quad (4.8)$$

and

$$q_3(\infty) = \int_{r_3}^{r_4} dr\, \bar{A}'(r)A''(r)A_i(t')\cos\theta''(r), \quad (4.9)$$

where

$$t' \equiv (2n'+1)^{2/3}\phi(r'),$$
$$t'' = (2n''+1)^{2/3}\phi(r''), \quad (4.10)$$

$$A'(r) = C'_{n'}|\phi'(r')|^{-\frac{1}{6}}(dr/ds)^{\frac{1}{2}}M'(z'), \text{ etc.}, \quad (4.11a)$$

and

$$\bar{A}''(r) = C''_{n''}|\phi(r'')|^{-\frac{1}{6}}(dr/ds)^{\frac{1}{2}}, \text{ etc.}, \quad (4.11b)$$

with $\phi(r')$ and $\phi(r'')$ being the phase integrals in terms of the initial and final state potential curve, respectively. The symbol ∞ in $q_i(\infty)$ signifies the large n limit.

For large n' and n'', the functions $\cos\theta'$ and

$\cos\theta''$ are very rapidly oscillating functions of r within the respective two classical turning points and the number of nodes depends on the vibrational quantum number.

Let us consider (4.8) first. Since the integrand in (4.8) is a rapidly oscillating function of r, the major contribution to the integral comes from the region of r where there is a stationary phase point. In order to exploit this point, let us write (4.8) in the form;

$$q_2(\infty) = \frac{1}{4}\int_{r_2}^{r_3} dr\, A'(r)A''(r)$$
$$\{\exp[i(\theta'+\theta)] + \exp[i(\theta-\theta'')]$$
$$+C.C.\}. \quad (4.12)$$

If there exists a stationary phase point r_s such that

$$\left[\frac{d}{dr}(\theta'-\theta'')\right]_{r=r_s} = 0, \quad (4.13)$$

we may approximate the phase around the point r_s by the formula,

$$\theta'-\theta'' = (\theta'-\theta'')_{r=r_s} + \alpha(r-r_s)^2, \quad (4.14)$$

where

$$\alpha = \frac{1}{2}\left[\frac{d^2}{dr^2}(\theta'-\theta'')\right]_{r=r_s}. \quad (4.15)$$

If the stationary phase point is defined by (4.13), then the integral including the phase $\theta'+\theta''$ does not have a stationary phase point and hence will be negligibly small compared with that having a stationary point. Since $A'(r)$ and $A''(r)$ are slowly varying smooth functions of r, we may regard them as constant around r_s. Then following the usual procedure in the method[12] of stationary phase, we obtain for $q_2(\infty)$ the following result:

$$q_2(\infty) \approx \frac{1}{2}(\pi/\alpha)^{\frac{1}{2}}A'(r_s)A''(r_s) \cdot$$
$$\cos[\Delta\theta(r_s)+\pi/4], \quad (4.16)$$

where

$$\Delta\theta(r_s) = \theta'(r_s) - \theta''(r_s). \quad (4.17)$$

Before we evaluate the integrals (4.7) and (4.9), let us consider the physical significance of the condition (4.13) above. For this purpose, it is useful to note the asymptotic formulas[8] of $\theta(t)$ and $M(t)$,

$$\theta(t) \sim \frac{1}{4}\pi - \frac{2}{3}t^{3/2}\Big[1 - \frac{5}{4}(2t)^{-3}$$
$$+ \frac{1105}{96}(2t)^{-6} - \cdots\Big], \qquad (4.18)$$

$$M^2(t) \sim \pi^{-1}t^{-\frac{1}{2}}\sum_{k=0}^{\infty}\frac{(-1)^k}{12^k k!}2^{3k}\Big(\frac{1}{2}\Big)_{3k}(2t)^{-3k}. \qquad (4.19)$$

Therefore, if we truncate (4.18) at the leading term, we obtain for θ' and θ''

$$\theta = \lambda \int_{r_0}^{r} dr' p(r') - \pi/4, \qquad (4.20)$$

where r_0 is either r_1 or r_3. On substitution of (4.20) into (4.13), we finally obtain the following expression equivalent to (4.13),

$$[E'_{n'J'} - U'_{\text{eff}}(r_s)]^{\frac{1}{2}} = [E''_{n''J''} - U''_{\text{eff}}(r_s)]^{\frac{1}{2}} \qquad (4.21)$$

or

$$E'_{n'J'} - U'_{\text{eff}}(r_s) = E''_{n''J''} - U''_{\text{eff}}(r_s), \qquad (4.21a)$$

which is Mulliken's condition. However, it is to be noted that $r_2 \leqslant r_s \leqslant r_3$ in the present case. Since the physical implication of (4.21a) was thoroughly discussed in relation to Franck-Condon transition by Mulliken, we shall not dwell on it here. The condition more accurate than (4.21a) of course is (4.13), which may be put in the form,

$$[E'_{n'J'} - U'_{\text{eff}}(r_s)]^{\frac{1}{2}}t'^{-\frac{1}{2}}(r_s)M'^{-2}[t'(r_s)]$$
$$= [E''_{n''J''} - U''_{\text{eff}}(r_s)]^{\frac{1}{2}}t''^{-\frac{1}{2}}(r_s) M''^{-2}[t''(r_s)]. \qquad (4.22)$$

We have made use of (2.22) to obtain (4.22). It is easy to see that (2.22) reduces to (4.17) when we retain only the first term in (4.19),

which is equal to 1.

Now we shall consider (4.7) and (4.9). Since the Airy functions $A_i(t')$ and $A_i(t'')$ are non-oscillating functions in the respective region of integration, there is only one oscillating function in each integral. Here again we may resort to the method of stationary phase for evaluation of the integrals. Since both integrals may be evaluated in the same method, we will consider only one integral, e.g., (4.7). The major contribution to the integral will come from the region around the stationary phase point r_s' defined this time by

$$\Big[\frac{d}{dr}\theta'(r)\Big]_{r=r_s'} = 0. \qquad (4.23)$$

This implies that the stationary phase point, r'_s is located approximately at the classical turning point r_1 (see (4.20)). Therefore, we obtain for the integral

$$q_1(\infty) \approx \frac{1}{2}(\pi/\alpha')^{\frac{1}{2}}A'(r_s')\bar{A}''(r_s')$$
$$A_i[t''(r_s')]\cos[\theta'(r_s') + \pi/4], \qquad (4.24)$$

where

$$\alpha' = \frac{1}{2}\Big[\frac{d^2}{dr^2}\theta'\Big]_{r=r_s'}. \qquad (4.25)$$

Similarly, we obtain for $q_3(\infty)$

$$q_3(\infty) \approx \frac{1}{2}(\pi/\alpha'')^{\frac{1}{2}}\bar{A}'(r_s'')A''(r_s'')$$
$$A_i[t'(r_s'')]\cos[\theta''(r_s'') + \pi/4], \qquad (4.26)$$

where

$$\alpha'' = \frac{1}{2}\Big[\frac{d^2}{dr^2}\theta''\Big]_{r=r_s''}. \qquad (4.26a)$$

If $r \leqslant r_2$ and $r_3 \leqslant r_4$ then the magnitudes of $q_1(\infty)$ and $q_3(\infty)$ are much smaller than that of $q_2(\infty)$, since we have the following inequalities due to the exponentially decreasing Airy functions,

$$|\bar{A}'A_i(t')| \leqslant |A'|$$

and

$$|\bar{A}''A_i(t'')| \ll |A''|.$$

Therefore, $q_1(\infty)$ and $q_3(\infty)$ may be neglected in comparison with $q_2(\infty)$ in (4.3). If $r_1 \approx r_2$ and $r_3 \approx r_4$ then $q_1(\infty)$ and $q_3(\infty)$ are equal to zero (see (4.3)). Therefore, in either case, q may be given by

$$q \approx q_2(\infty)$$

and thus the Franck-Condon factor by

$$Q(\infty) \approx (\pi/4|\alpha|)[A'(r_s)A''(r_s)]^2$$
$$\cos^2[\Delta\theta(r_s) + \pi/4]. \qquad (4.27)$$

Now we consider the case when the initial state is in the ground vibrational-rotational state. The corresponding wavefunction is then a smooth nonoscillating function of r. If the transition is to a high vibrational state of the final state, then we may approximate q by the formula

$$q(\infty) \approx \int_{r_2}^{r_4} dr \, u^{(0)\prime}(00, r)A''(r)\cos\theta''(r) \cdot \qquad (4.28)$$

We have neglected the region $[0, r_2]$ and $[r_4, \infty]$ to obtain (4.28). Again this integral can be evaluated by means of the stationary phase approximation. The result is

$$q(\infty) \approx \frac{1}{2}(\pi/\alpha'')^{\frac{1}{2}}u^{(0)\prime}(00, r_s)A''(r_s) \cdot$$
$$\cos\theta''(r_s) \qquad (4.29)$$

Where

$$\alpha'' = \frac{1}{2}\left[-\frac{d^2}{dr^2}\theta''\right]_{r=r_s'}.$$

In this case, we obtain for the stationary phase point a condition similar to (4.25),

$$\left(\frac{d\theta''}{dr}\right)_{r=r_s} = 0 \qquad (4.30)$$

or

$$t''^{-\frac{1}{2}}(r_s)M''^{-2}[t''(r_s)][E''_{n''J''} - U''_{\text{eff}}(r_s)]^{\frac{1}{2}}$$

$$= 0$$

which implies

$$E''_{n''J''} - U''_{\text{eff}}(r_s) = 0. \qquad (4.31)$$

Thus, the transition happens vertically to the relative nuclear coordinate corresponding to the classical turning point of the final state. This coincides with the original idea of the Franck-Condon principle. In this regard, it is interesting to see *Fig.* 3a where the probability amplitude has almost a Gaussian shape around the turning point of the upper state and such Gaussian function may be approximated by a delta function. The same procedure applies to the reverse case in which the initial state is a high vibrational state while the final state is in the ground state.

In summary, in this article we have shown that the uniform WKB solution for a two-turning point problem is very accurate and thus should be useful for studies of various molecular processes[13]. As an example for such processes, the Franck-Condon transitions for $A_2 \rightarrow A_2^+$ are considered and the transition probabilities are calculated. We have also derived Mulliken's frequency condition which was orginally obtained, based on physical arguments. The derivation is achieved by using the uniform WKB wavefunction and the stationary phase method[12] provides its mathematical basis.

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