Analytical Evaluation of Two-Center Franck-Condon Overlap Integrals over Harmonic Oscillator Wave Function

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A unified treatment of Franck-Condon (FC) overlap integrals with arbitrary values of parameters is described. These integrals are represented in terms of binomial coefficients. For quick calculations, the binomial coefficients are stored in the memory of the computer. Therefore, the CPU time has been greatly reduced. Numerical results presented agree excellently with those obtained in the literature.

Key words: Franck-Condon Factors; Harmonic Oscillator Wave Function; Overlap Integral; Binomial Coefficients.

1. Introduction

The Franck-Condon (FC) overlap integrals between two electronic states, whose squares are the so-called FC factors, determine the transition probabilities of various vibrational levels and the intensities of various lines in the spectra of molecules [1 – 18]. In the literature, various efficient methods have been proposed for improving the evaluation of the FC overlap integral of two harmonic wave functions in the harmonic approximation [19 – 30]. Accurate values of FC factors and related quantities obtained by FC overlap integrals are essential to obtain the radiative life time and vibrational temperature of astrophysical molecules [31 – 34], interpretation of polyatomic photodissociation [35 – 37], predissociation [38], collision induced dissociation [39] and reaction dynamics [40 – 46]. For the calculation of FC overlap integrals, new analytic formulae have been proposed [20 – 23, 47 – 50]. The purpose of this paper is to present the analytic formulae for FC overlap integrals over harmonic oscillator wave functions that contain simple finite sums of binomial coefficients which can be easily evaluated for any n and n'. These relations are especially useful for the computation of FC factors which essentially involve the overlap integral between wave functions of vibrational levels belonging to two different electronic states of a molecule. It should be noted that the accurate evaluation of the FC overlap integrals gives the molecular structure information needed to evaluate the band intensities in emission and absorption [51 – 56] and to use in the application of narrow band tunable lasers [57 – 59].

2. Definition and Analytical Relation for Franck-Condon Overlap Integrals

The two-center FC overlap integrals of harmonic oscillator wave functions centered at different equilibrium positions have the following form:

$$I_{m'}(\Delta;\alpha,\alpha') = \int_{-\infty}^{\infty} \psi_n(\alpha;x)\psi_{n'}(\alpha';x-\Delta)\,\mathrm{d}x, \quad (1)$$

where $x' = x - \Delta$ and $\psi_n(\alpha;x)$ are the normalized harmonic oscillator wave functions defined by

$$\psi_n(\alpha;x) = \sqrt{\frac{\alpha}{\sqrt{\pi}2^n n!}}\,\mathrm{e}^{-\alpha^2x^2/2}H_n(\alpha x). \quad (2)$$

Here, α is related to the frequency ω by $\alpha = (\mu\omega/\hbar)^{1/2}$ and $H_n(\alpha x)$ are the Hermite polynomials determined by [60]

$$H_n(\alpha x) = \sum_{s=0}^{[n/2]} (-1)^s F_s(n) F_s(n-s) s! (2\alpha x)^{n-2s}, \quad (3)$$

where $F_s(n) = n!/[s!(n-s)!]$ is the binomial coefficient.

Substituting the Hermite polynomials (3) into (1), we get for the FC overlap integrals in terms of binomial

coefficients the relation

$$I_{nn'}(\Delta;\alpha,\alpha') = \sqrt{\frac{\alpha}{\sqrt{\pi}2^n n!}}\sqrt{\frac{\alpha'}{\sqrt{\pi}2^{n'}n'!}}\sum_{s=0}^{[n/2]}(-1)^s F_s(n)F_s(n-s)s!\sum_{s'=0}^{[n'/2]}(-1)^{s'}F_{s'}(n')F_{s'}(n'-s')s'! \cdot Q_{n-2s,n'-2s'}(\Delta;\alpha,\alpha') \tag{4}$$

where $[n/2] = \frac{n}{2} - \frac{1}{4}[1-(-1)^n]$ and

$$Q_{nn'}(\Delta;\alpha,\alpha') = 2^{n+n'}\alpha^n(\alpha')^{n'}\int_{-\infty}^{\infty} x^n(x-\Delta)^{n'}\mathrm{e}^{-\alpha^2x^2/2}\mathrm{e}^{-\alpha'^2(x-\Delta)^2/2}\,\mathrm{d}x. \tag{5}$$

The FC overlap integrals (4) have the symmetry property

$$I_{nn'}(\Delta;\alpha,\alpha') = (-1)^{n+n'}I_{n'n}(\Delta;\alpha',\alpha). \tag{6}$$

In order to evaluate the auxiliary functions $Q_{nn'}$ occurring in (4) and (5) we use the binomial expansion theorem. Then we find for the auxiliary functions $Q_{nn'}$ the relation

$$Q_{nn'}(\Delta;\alpha,\alpha') = 2^{n+n'}\alpha^n(\alpha')^{n'}\mathrm{e}^{-\alpha'^2\Delta^2/2}\sum_{m=0}^{n'}(-1)^m F_m(n')\Delta^m K_{n+n'-m}(\alpha_1,\alpha_2), \tag{7}$$

where $\alpha_1 = \frac{(\alpha^2+\alpha'^2)}{2}$, $\alpha_2 = \frac{\alpha'^2\Delta}{2}$, and K_n is the basic integral defined by [60]

$$K_n(p,q) = \int_{-\infty}^{\infty} x^n\mathrm{e}^{-px^2+2qx}\mathrm{d}x = n^1\mathrm{e}^{q^2/p}\sqrt{\frac{\pi}{p}}\left(\frac{q}{p}\right)^n\sum_{k=0}^{[n/2]}\frac{1}{(n-2k)!k!}\left(\frac{p}{4q^2}\right)^k \quad \text{for } p>0. \tag{8}$$

The absorption and emission processes can be determined from the FC overlap integrals by the relations [19–51]

$$R_{n,n'} \propto \nu_{n,n'}|I_{n\to n'}|^2 \quad \text{(absoprtion)}, \tag{9}$$

$$R_{n,n'} \propto \nu^4_{n,n'}|I_{n\to n'}|^2 \quad \text{(emission)}, \tag{10}$$

where the phase-space factor of $\nu^4_{n,n'}$ embodies the characteristic $\nu^3_{n,n'}$ dependence of the spontaneous emission probability combined with an extra factor $\nu_{n,n'}$ that reflects the frequency scaling of the quantum yield for a photon detector having constant radiant sensitivity [56]. As seen from (9) and (10), the problem of the absorption and emission determinations reduces to the numerical calculation of the FC overlap integral given in (4).

For the quick calculations of FC overlap integrals, the binomial coefficients are stored in the memory of the computer. For this purpose we use the recurrence relation

$$F_m(n) = F_m(n-1) + F_{m-1}(n-1), \tag{11}$$

where $F_0(n) = 1$ and $F_m(n) = 0$ for $m<0$, $m>n$. In order to put the binomial coefficients into the memory or to get them back, the position of the coefficient $F_m(n)$ is determined by [61–63]

$$F(n,m) = n(n+1)/2 + m + 1. \tag{12}$$

3. Numerical Results and Discussion

In this paper, an analytical formula has been derived for the calculation of the two-center FC overlap integral over harmonic oscillator wave functions which can be used only in the case of a non-degenerate and harmonic vibrational degree of freedom, where the coupled electronic states have analogous equilibrium structures. The treatment of polyatomic transitions between linear and bent configurations of the molecular framework is prohibited by the above mentioned restrictions. We constructed a program for evaluating the FC overlap integrals on the basis of (4) obtained in this paper and (6) and (9) of the articles [56]

Table 1. The values of FC overlap integrals over harmonic oscillator wave functions.

n	n'	α	α'	Δ	Mathematica 5.0 for (4)	Turbo Pascal 7.0 for (4)	(9) in [52]
0	2	0.001	3	1.6	1.825739014253E-02	1.825739014253E-02	1.825739014253E-02
7	0	4	0.002	2.1	1.389004582840E-07	1.389004582840E-07	1.389004582840E-07
5	3	0.15	0.13	3	3.551660830446E-01	3.551660830446E-01	3.551660830446E-01
2	10	2	1.3	4	2.366315187074E-01	2.366315187072E-01	2.366315187072E-01
15	2	7	0.003	0.9	−3.002533163170E-07	−3.002533163170E-07	−3.002533163170E-07
12	15	3.1	3	3.8	−1.525128270577E-02	−1.525128294622E-02	−1.525128294672E-02
20	4	0.9	1.8	3.5	2.824038713409E-01	2.824038571984E-01	2.824038571999E-01
16	1	0.02	0.0003	1.6	−5.152490060391E-05	−5.152490060393E-05	−5.152490060393E-05
7	8	3	1	3.2	−2.775548581730E-02	−2.775548581738E-02	−2.775548581738E-02
1	40	2.7	0.19	0.12	1.983655888171E-02	1.983655888171E-02	1.983655888171E-02
18	20	0.016	1	3	2.514935209191E-02	2.514869577348E-02	2.514869568556E-02
30	30	1.52	0.37	2.4	3.153193418755E-02	3.15310563300E-02	3.153105367625E-02
2	0	0.0001	0.003	1	1.820677904777E-01	1.820677904777E-01	1.820677904777E-01
30	20	10	13	6	2.533929533760E-433	2.533929601159E-433	2.533929533759E-433
44	3	0.29	5.6	2	5.118391295484E-02	5.118391295835E-02	5.118391295836E-02
18	24	0.081	0.0076	3.46	−4.923959622501E-02	−4.923959622471E-02	−4.923959622471E-02
20	20	12.3	4.5	1.25	1.264148486267E-02	1.264954076045E-02	1.264953711653E-02
25	25	5.7	0.15	2	−1.906941068675E-02	−1.906941068383E-02	−1.906941068382E-02
20	10	10	12	10	6.84570859069E-1238	6.84570859068E-1238	6.84570859068E-1238

and [52], respectively. The calculation programs were performed on a computer Pentium III, 80 MHz (using Turbo Pascal Language) in double precision with an accuracy of significant digits and Mathematica 5.0 international mathematical software. The computer calculations, based on the use of (4), the analytical relations for FC overlap integrals show great numerical stability. The calculated results of these equations for various parameters are presented in Table 1.

As can be seen in Table 1, the calculated values of FC overlap integrals over harmonic oscillator wave functions show a good rate of convergence with literature in the range of parameters. Our results are in excellent agreement with the results of Mathematica 5.0 international mathematical software. The results obtained from (4) of this study and (9) of [52] for a given α, α' and Δ are satisfactory for the n and n' values. They deteriorate as n and n' increase. As discussed in [19, 56], (9) of [52] can be adapted to approximate the one-dimensional anharmonic overlap integrals. It should be noted that the inverse procedure of contraction (expansion) can be used to go from harmonic to anharmonic oscillators.

In this paper we present a computer program code in the Appendix of the Mathematica 5.0 international mathematical software, which evaluates the general FC overlap integrals in terms of binomial coefficients. The program can be used by students since it does not require any knowledge of higher-level mathematics.

Appendix

The program is written in Mathematica 5.0 international mathematical software according to the algorithm described above. The listing of the program is as follows:

```
Kn[n_, p_, q_] := n! Exp[q^2/p] Sqrt[π/p] (q/p)^n *

   Sum[ 1/((n - 2k)! k!) (p/(4 q^2))^k,
     {k, 0, ((n/2) - 1/4 (1 - (-1)^n))}];

Qnn1[n_, n1_, d_, a_, a1_] := Module[{a2, a3},
   a2 = (a^2 + a1^2)/2; a3 = (a1^2) d/2;
   2^(n + n1) (a^n) (a1^n1) / Exp[(a1 * d)^2/2] *
    Sum[(-1)^m * Binomial[n1, m] d^m * Kn[n + n1 - m, a2, a3],
     {m, 0, n1}]];

Condon[n_, n1_, a_, a1_, d_] :=
  Module[{An, An1}, An = Sqrt[ a/(Sqrt[π] 2^n (n!)) ];
   An1 = Sqrt[ a1/(Sqrt[π] 2^n1 (n1!)) ];
   An * An1 *
    Sum[(-1)^s * Binomial[n, s] Binomial[n - s, s] s! *
      (-1)^s1 * Binomial[n1, s1] Binomial[n1 - s1, s1]
      s1! * Qnn1[n - 2s, n1 - 2s1, d, a, a1],
     {s, 0, ((n/2) - 1/4 (1 - (-1)^n))},
     {s1, 0, ((n1/2) - 1/4 (1 - (-1)^n1))}]];
n = 2; n1 = 1; a = 4; a1 = 3; d = 2;
NumberForm[N[Condon[n, n1, a, a1, d]], 60]
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