Overlap Integrals and Recursion Formulas for Morse Wavefunctions

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Overlap integrals for the case in which the ground and excited states are represented by Morse potential functions were derived. In order to calculate the spectral intensities in Morse wavefunctions, a method of expanding the wavefunctions of one state in terms of the other was developed to allow the ground and the excited state frequencies to be different. From the expansion of Morse wavefunctions, recursion formulas were developed for variational matrix elements of Morse wavefunctions. The matrix elements can be calculated using these recursion formulas and the diagonalized results which eigenvalues (allowed energies) were all successfully satisfied to Morse energy formulas.

Introduction

Spectral intensities in absorbances, fluorescence, Raman and CARS (coherent Anti-stokes Raman Spectroscopy) at a given wavelength depend upon several molecular parameters such as ground and excited state frequencies, dissociation energies, and displacement of the excited state along the normal coordinate of interest.

Inagaki, *et al.*[1] have evaluated the approximate overlap integrals for the case in which both the ground and excited electronic states are harmonic and identical, but displaced from each other along the normal coordinate of interest. Therefore the ground state and excited state frequencies must be equal which limits the generality of the treatment. The treatment on Harmonic oscillator was then significantly improved by Berkowitz[2] by allowing the ground and excited state frequencies to differ. With these results, Carreira *et al.*[3] have tested the excitation profiles of N,N-diethyl-p-nitrosoaniline, Potassium Permanganate and Potassium Chromate using the program, and they have produced a satisfactory excitation profile of the above molecules.

A thorough search of the literature revealed no closed form evaluations of overlap integrals of Morse wavefunctions. In this report we have developed overlap integrals for Morse potential wavefunctions in which excited state frequency and dissociation energy are equal to ground state frequency and dissociation. Also, we developed relation for variational matrix elements of Morse wavefunctions when frequency and dissociation energy of excited states differ with those of ground states.

A program has been developed to calculate the energy levels and corresponding wavefunctions for Morse potential wavefunctions.

Morse wave functions for the nuclear vibration

The Morse potential function in terms of displacement from the equilibrium position r_0 is given[4] by

$$V_{(r)} = De^{-2a(r-r_0)} - 2De^{-a(r-r_0)} \tag{1}$$

where

$$a = \left(\frac{8\pi^2 c\mu w_0 x_0}{h}\right)^{1/2}$$

w_0x_0 = Spectroscopic anharmonicity factor in cm^{-1}

D = dissociation energy

The wavefunction derived from this potential are given[4] by

$$\psi_n(r) = \left(\frac{2da}{N_n}\right)^{1/2} e^{-de^{-a(r-r_0)}} [2de^{-a(r-r_0)}]^{(k-2n-1)/2} L^{k-2n-1}_{k-n-1} [2de^{-a(r-r_0)}] \tag{2}$$

where

$$d = 2\pi(2\mu D)^{1/2}/ah, \quad k = 2d = 4\pi(2\mu D)^{1/2}/ah$$

L^b_a = associated Laguerre Polynomial of degree b–a

$Nn = [(k-n-1)!]^2 \sum_{s=0}^{n} \frac{(k-2n+s-2)!}{S!}$ (Nn represents the nomalization constant given by Morse[4] for integral K)

Transforming to the dimensionless coordinate, ξ, equation (1) and (2) become (3) and (4)

$$V(\xi) = De^{-2a'\xi} - 2De^{-a'\xi} \tag{3}$$

$$\psi_n(\xi) = \left(\frac{2da}{Nn}\right)^{1/2} e^{-de^{-a'\xi}} [2de^{-a'\xi}]^{\beta n/2} L^{\beta n}_{\beta n+n} (2de^{-a'\xi}) \tag{4}$$

where

$$\beta_n = k-2n-1, \quad a' = (\mu\gamma)^{-1/2} a, \quad \xi = (\mu\gamma)^{1/2}(r-r_0),$$

$$\gamma = \frac{4\pi^2\nu}{h} \text{ and } \mu = \text{reduced mass}$$

If the potential well equilibrium position is displaced by Δ, Ψ_n is given by;

$$\begin{aligned} \psi_n(\xi-\Delta) &= \left(\frac{2da}{Nn}\right)^{1/2} e^{-de^{-a'(\xi-\Delta)}} [2de^{-a'(\xi-\Delta)}]^{\beta n/2} L^{\beta n}_{\beta n+n} [2de^{-a'(\xi-\Delta)}] \\ &= \left(\frac{2da}{Nn}\right)^{1/2} e^{-de^{-a'\xi}e^{a'\Delta}} [2de^{-a'\xi}e^{a'\Delta}]^{\beta n/2} L^{\beta n}_{\beta n+n} [2de^{-a'\xi}e^{a'\Delta}] \end{aligned} \tag{5}$$

To simplify the forms of equations (3), (4), (5) following substitutions were made; $X = 2de^{-a'\xi}$, $c = e^{a'\Delta}$

$$V(x) = \frac{D}{4d^2}X^2 - \frac{D}{d}X \tag{6}$$

$$\Phi_{i,g}(X) = \left(\frac{2da}{Ni}\right)^{1/2} e^{-X/2} X^{\beta i/2} L^{\beta i}_{\beta i+i}(X) \tag{7}$$

$$\psi_{v,e}(CX) = \left(\frac{2da}{Nv}\right)^{1/2} e^{-CX/2} (CX)^{\beta v/2} L^{\beta v}_{\beta v+v}(CX) \tag{8}$$

where the following notations are used;

$\Phi_{i,g}$ represent ground state wave functions, $\Psi_{v,e}$ represent excited state wavefunctions.

Overlap integrals with Morse wavefunction.

A. excited state frequency and dissociation energy equal to ground state frequency and dissociation energy.

The first step in the evaluation of the overlap integral involves the transformation to dimensionless coordinate X defined earlier.

$$X=2de^{-a'\xi},\ \xi=(\mu\gamma)^{1/2}r$$
$$d\xi=(\mu\gamma)^{1/2}dr$$
$$dx=-a'2de^{-a'\xi}d\xi=-a'Xd\xi=-a'(\mu\gamma)^{1/2}Xdr$$

remembering that $a'=a(\mu\gamma)^{-1/2}$ and rearranging;

$$dr=-\frac{1}{a}\frac{dx}{x}$$

Therefore;

$$\int\Phi_i^*(r)\psi_v(r-\Delta)dr=-\frac{1}{a}\int X^{-1}\Phi_i^*(X)\psi_v(CX)dx \quad (9)$$

combining equations (7), (8) and (9) gives

$$\langle i|v\rangle=\frac{-2dc^{\beta_v/2}}{(N_iN_v)^{1/2}}\int e^{-(1+C)X/2}X^{(\beta_i+\beta_v-2)/2}L^{\beta_i}_{\beta_i+i}(X)L^{\beta_v}_{\beta_v+v}(CX)dx \quad (10)$$

This integral is evaluated using a method based on related work done by Schroedinger.[5] This is identical in form to Schroedinger's equation if the following definitions are made;

$$\alpha_s=1,\ \beta_s=C,\ n_s=\beta_i,\ K_s=i,\ n'_s=\beta_v,\ K'_s=V,$$
$$p=(\beta_i+\beta_{v-2})/2$$

Rewriting equation (10) in terms of these definitions give;

$$\langle i|v\rangle=\frac{-2d\beta_s^{n_s'/2}}{(N_iN_v)^{1/2}}\int e^{-(\alpha_s+\beta_s)X/2}X^pL^{n_s}_{n_s+k_s}(\alpha_sX)L^{n'_s}_{n'_s+k'_s}(\beta_sX)dX$$
$$=\frac{-2d\beta_s^{n'_s/2}}{(N_iN_v)^{1/2}}J_s \quad (11)$$

Schroedinger makes the following definitions:

$$y=\frac{\alpha_s+\beta_s}{2}X,\quad \sigma_s=\frac{2}{(\alpha_s+\beta_s)},\quad \gamma_s=(\alpha_s-\beta_s)/(\alpha_s+\beta_s)$$

Therefore
$$X=\sigma_s y$$
$$dX=\sigma_s dy$$
$$\alpha sX=(1+\gamma_s)y=y+\gamma_s y$$
$$\beta sX=(1-\gamma_s)y=y-\gamma_s y$$

Substitution into equation (11) gives;

$$J_s=\sigma_s^{P+1}\int_0^\infty y^Pe^{-y}L^{n_s}_{n_s+k_s}(y+\gamma_sy)L^{n'_s}_{n'_s+k'_s}(y-\gamma_sy)dy \quad (12)$$

Evaluation of the integral J_s depends upon the expansion of terms of the form $L^b_a(A+B)$.

B. Evalvation of J_s integral

In order to further evaluate equation (12), expansion of the Laguerre Polynomial evaluated at a sum of two functions of y must be derived. Buchholz[6] gives an equation for the expansion of terms of the form $L^b_a[A(y)+B(y)]$ into terms of $L^b_a[A(y)]$ and $L^b_a[B(y)]$ which is modified here to fit Schroedinger's equation (12). From the context in which it was used, the polynomial used in Schroedinger's paper, denoted by ${}_sL^b_n(y)$, is a possible solution to the differential equation (13).[7]

$$yZ''(y)+(b-y+1)Z'(y)+(a-b)Z(y)=0 \quad (13)$$

Buchholz defines the polynomial to be denoted as ${}_BL^b_n(y)$ in terms of equation (14).[6]

$$yZ''(y)+(b-y+1)Z'(y)+nZ(y)=0 \quad (14)$$

The two equations yield the following respective definitions of the polynomial for integral a and b.[7]

$${}_sL^b_a(y)=\frac{d^b}{dy^b}[e^y\frac{d^a}{dy^a}(y^ae^{-y})] \quad (15)$$

Equations (13) and (14) are identical if $n=a-b$

${}_BL^b_n(y)=L^b_{a-b}(y)$ and ${}_sL^b_a(y)$ can be expanded in powers of y[4,5]

$${}_sL^b_a(y)=\sum_{k=0}^{a-b}(-1)^{k+1}\frac{(a!)^2}{(a-b-k)!\,(b+k)!\,k!}y^k \quad (16)$$

$${}_BL^b_{a-b}(y)=\sum_{k=0}^{a-b}\binom{a}{a-b-k}\frac{y^k}{k!}$$
$$=a!\sum_{k=0}^{a-b}(-1)^k\frac{y^k}{(a-b-k)!\,(b+k)!\,k!} \quad (17)$$

comparing (16) with (17), it is clear that

$$-a!\,{}_BL^b_{a-b}(y)={}_sL^b_a(y) \quad (18)$$

Buchholz's equation for the expansion of ${}_BL^b_{a-b}[A(y)+B(y)]$ is given by

$${}_BL^b_{a-b}(A+B)=\sum_{\lambda=0}^{a-b}\frac{(-B)^\lambda}{\lambda!}{}_BL^{b+\lambda}_{a-b-\lambda}(A) \quad (19)$$

Combining equations (18) with (19) gives:

$${}_sL^b_a(A+B)=\sum_{\lambda=0}^{a-b}\frac{(-B)^\lambda}{\lambda!}{}_sL^{b+\lambda}_a(A) \quad (20)$$

From equation (20), it can be shown that:

$${}_sL^{n_s}_{n_s+K_s}(y+\gamma_sy)=\sum_{\lambda_s=0}^{K_s}\left(\frac{(-\gamma_sy)^{\lambda_s}}{\lambda_s!}\right){}_sL^{n_s+\lambda_s}_{n_s+K_s}(y) \quad (21)$$

$${}_sL^{n'_s}_{n'_s+K'_s}(y-\gamma_sy)=\sum_{\mu_s=0}^{K'_s}\left(\frac{(\gamma_sy)^{\mu_s}}{\mu_s!}\right){}_sL^{n'_s+\mu_s}_{n'_s+K'_s}(y) \quad (22)$$

Substitution into equation (12) and rearrangement gives:

$$J_s=\sigma_s^{P+1}\sum_{\lambda_s=0}^{K_s}\sum_{\mu_s=0}^{K'_s}(-1)^{\lambda_s}\frac{\gamma_s^{\lambda_s+\mu_s}}{\lambda_s!\,\mu_s!}\int_0^\infty y^{P+\lambda_s+\mu_s}e^{-y}\,{}_sL^{n_s+\lambda_s}_{n_s+K_s}(y)\,{}_sL^{n'_s+\mu_s}_{n'_s+K'_s}(y)dy \quad (23)$$

Now we can expand integral part.

$$J_s=\sigma_s^{P+1}\sum_{\lambda_s=0}^{K_s}\sum_{\mu_s=0}^{K'_s}(-1)^{\lambda_s}\frac{\gamma_s^{\lambda_s+\mu_s}}{\lambda_s!\,\mu_s!}K_{\lambda_s,\mu_s} \quad (24)$$

$$K_{\lambda_s,\mu_s}=(p+\lambda_s+\mu_s)!\,(n_s+k_s)!\,(n'_s+k'_s)!\sum_{\tau=0}^{\leq K'_s-\mu_s,\ K_s-\lambda_s}M_{\lambda_s,\mu_s,\tau} \quad (25)$$

$$M_{\lambda_s,\mu_s,\tau}=(-1)^{n_s+n'_s+K_s+K'_s+\tau}\binom{P+\mu_s-n_s}{K_s-\lambda_s-\tau}\binom{P+\lambda_s-n'_s}{K'_s-\mu_s-\tau}\binom{-P-\lambda_s-\mu_s-1}{\tau} \quad (26)$$

where n_s, k_s, n'_s, k'_s and P and defined earlier.

Thus, the total overlap integral $\langle i|v\rangle$ is given by

$$\langle i|v\rangle=\frac{-2dc^{\beta_v/2}}{(N_iN_v)^{1/2}}J_s \quad (27)$$

Calculation of overlap integrals in the case of $\Delta=0$ using equation (27) led to the following results:

$$\langle i|v\rangle = K\delta_{iv}; \quad \begin{array}{l}\delta_{iv}=1, \ i=v \\ \delta_{iv}=0, \ i\neq v\end{array} \tag{28}$$

Thus to fully normalize the wavefunctions, the normalization constant is redefined by:

$$N'_n = [k^{1/2}(k-n-1)!]^2 \sum_{s=0}^{n} \frac{(k-2n+S-2)!}{s!} = kNn \tag{29}$$

Values of the relevant terms are given in Table 1 for specific integrals of interest. (excited state frequency and dissociation energy equal to ground state frequency and dissociation energy).

Since the Laguerre polynomials are only real when a and b are integers[4] the calculated value of k which typically ranges from 50 to 1000, is rounded to the nearest integer for the purpose of calculation, without significant loss of accuracy or generality.

Recursion formula for variational matrix elements of Morse wavefunctions. ($\nu_e \neq \nu_g$, $D_g \neq D_e$)

A. Excited state frequency and dissociation energy not equal to ground state frequency and dissociation energy.

The Morse potential function expressed in dimensionless coordinate, ξ is given by equation (3). Clearly, for the case in which these parameters differ in the excited and ground states, the potential functions will differ. Thus the potential functions for the ground and excited states are given by:

$$V_g(\xi) = D_g e^{-2a'_g\xi} - 2D_g e^{-a'_g\xi} \tag{30}$$

$$V_e(\xi') = D_e e^{-2a'_e\xi'} - 2D_e e^{-a'_e\xi'} \tag{31}$$

The respective wavefunctions of the two states will then be given by:

$$\Phi_{i,g}(\xi)$$

$$= \left(\frac{2d_g a_g}{N_i}\right)^{1/2} e^{-d_g e^{-a'_g\xi}} [2d_g e^{-a'_g\xi}]^{\beta_{i,g}/2} \ {}_sL^{\beta_{i,g}}_{\beta_{i,g}+i} (2d_g e^{-a'_g\xi}) \tag{32}$$

$$\psi_{v,e}(\xi')$$

$$= \left(\frac{2d_e a_e}{N'_v}\right)^{1/2} e^{-d_e e^{-a'_e\xi'}} [2d_e e^{-a'_e\xi'}]^{\beta_{v,e}/2} \ {}_sL^{\beta_{v,e}}_{\beta_{v,e}+v} (2d_e e^{-a'_e\xi'}) \tag{33}$$

where $\Phi_{i,g}$ is the wavefunction of the i^{th} level in the ground state and $\Psi_{v,e}$ *is the* V^{th} wavefunction in the excited state. Wavefunctions (32) and (33) are different but any arbitrary well-behaved function can be expanded in terms of the orthonormal eigenfunctions of a Hermitian operator. If the excited state frequency is greater than the ground state frequency, the excited state wavefunctions are expanded in terms of a basis set consisting of the ground state wavefunctions. Thus, for the case in which $\nu_e > \nu_g$ and $D_e \neq D_g$

Table 1. Evaluation of Important Integrals of Morse Wavefunctions

Integral	n_s	k_s	n'_s	k'_s	P
<O|V>	k-1	0	k-2V-1	V	k-V-1
<O|i>	k-2i-1	i	k-1	O	k-i-1
<V|1>	k-3	1	k-2V-1	V	k-V-2
<1|V>	k-3	1	k-2V-1	V	k-V-2
<V|0>	k-1	0	k-2V-1	V	k-V-1
<V|2>	k-5	2	k-2V-1	V	k-V-3
<2|V>	k-5	2	k-2V-1	V	k-V-3

i = ground state vibrational energy level. V = excited state vibrational energy level. 0,1,2 = vibrational energy level.

$$\psi_v = \sum_i C_{vi} \Phi_i \tag{34}$$

where the summation ranges over both even and odd values of i. For the case in which $\nu_e < \nu_g$,

$$\Phi_i = \sum_t C_{it} \psi_t \tag{35}$$

where the summation ranges over both even and odd values of t. Therefore, the overlap integrals of interest are of the form:

if $\nu_e > \nu_g$ and $D_e \neq D_g$

$$\langle i|V\rangle = \int \Phi^*_{i,g} \psi_{v,e} d\tau = \sum_m C_{vm} \langle i|m\rangle \tag{36}$$

$$\langle V|j\rangle = \int \psi^*_{v,e} \Phi_{j,g} d\tau = \sum_m C_{vm} \langle m|j\rangle \tag{37}$$

if $\nu_e < \nu_g$ and $D_e \neq D_g$

$$\langle i|V\rangle = \int \Phi^*_{i,g} \psi_{v,e} d\tau = \sum_t C_{it} \langle t|v\rangle \tag{38}$$

$$\langle V|j\rangle = \int \psi^*_{v,e} \Phi_{j,g} d\tau = \sum_t C_{jt} \langle v|t\rangle \tag{39}$$

Evaluation of the constants Cvm and Cit is necessary before the overlap integrals (36) → (39) can be used.

These constants Cvm and Cit are evaluated by the formation and diagonalization of a variational Hamiltonian matrix whose elements are given by:

$$H_{ij} = \int \Phi^*_{i,g} \hat{H}_e \Phi_{j,g} d\tau \quad (\nu_e > \nu_g;\ D_e \neq D_g) \tag{40}$$

Where $\Phi_{i,g}$ and $\Phi_{j,g}$ are ground state wave functions and $\hat{H}e$ is the Hamiltonian operator of the excited state defined by:

$$\hat{H}_e = \hat{T} + \hat{V}_e : \hat{T} = \frac{1}{2}\hat{P}^2 \tag{41}$$

$$H_{v,t} = \int \psi^*_{v,e} \hat{H}_g \psi_{t,e} d\tau \quad (\nu_e < \nu_g) \tag{42}$$

Where $\Psi_{v,e}$ and $\Psi_{t,e}$ are excited state wavefunctions and $\hat{H}_g$ is the Hamiltonian operator of the ground state defined by:

$$\hat{H}_g = \hat{T} + \hat{V}_g : \hat{T} = \frac{1}{2}\hat{P}^2 \tag{43}$$

Hamiltonian matrix elements are of the form (for eqn (40)):

$$H_{ij} = T_{i,j} + V_{ei,j} \tag{44}$$

where

$$T_{i,j} = \int \Phi^*_i \hat{T} \Phi_j d\tau$$

$$V_{ei,j} = \int \Phi^*_i \hat{V}_e \Phi_j d\tau$$

B. Coordinate Transformation of Hamiltonian and Wavefunctions.

The Hamiltonian of the excited state is given by

$$\hat{H}e(\xi') = \hat{T}(\xi') + \hat{V}_e(\xi') \tag{45}$$

In order to define the excited state potential (31) in terms of the ground state (30), the following definition is made:

$$t = \frac{a'_e\ \xi'}{a'_g\ \xi} \tag{46}$$

In order to keep ${}_sL^b_a$ real, as described earlier, t is rounded to the nearest integer. Thus:

$$\hat{V}_e(\xi') = D_e (e^{-a'_g\xi})^{2t} - 2D_e (e^{-a'_g\xi})^t \tag{47}$$

Rearrangement with dimensionless coordinate X, (47) gives:

$$\hat{V}_e(X)=AX^{2t}-BX^t \qquad (48)$$

where

$$X\equiv 2d_g e^{-a'_g\xi},\quad A=\frac{D_e}{(2d_g)^{2t}},\quad B=\frac{2D_e}{(2d_g)^t}$$

In terms of displacement from the equilibrium position $(r-r_0)$, the kinetic energy operator is given by:

$$\hat{T}=-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} \qquad (49)$$

From the earlier definition $\xi=(\mu\gamma)^{1/2}r,\ a'=a(\mu\gamma)^{-1/2}$

$$\frac{aX}{ar}=-a'(\mu\gamma)^{1/2}X \qquad (50)$$

$$\frac{\partial^2}{\partial r^2}=(\frac{\partial X}{\partial r}\frac{\partial}{\partial X})^2=\frac{\partial X}{\partial r}\frac{\partial}{\partial X}[-a'(\mu\gamma)^{1/2}X\frac{\partial}{\partial X}]$$

$$=a'^2(\mu\gamma)(X\frac{\partial}{\partial X}+X^2\frac{\partial^2}{\partial X^2}) \qquad (51)$$

Therefore;

$$\hat{T}=-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}=-\frac{ha'^2_g\nu}{2}[X\frac{\partial}{\partial X}+X^2\frac{\partial^2}{\partial X^2}] \qquad (52)$$

$$\hat{T}=E[X\frac{\partial}{\partial X}+X^2\frac{\partial^2}{\partial X^2}] \qquad (53)$$

where

$$E=-\frac{ha'^2_g\nu}{2}$$

$$\hat{T}=E(\hat{T}_1+\hat{T}_2) \qquad (54)$$

where

$$\hat{T}_1\equiv X\frac{\partial}{\partial X}\ \text{and}\ \hat{T}_2\equiv X^2\frac{\partial^2}{\partial X^2}$$

Thus;

$$\hat{T}\Phi_{n,g}=E(\hat{T}_1\Phi_{n,g}+\hat{T}_2\Phi_{n,g}) \qquad (55)$$

The wavefunction $\Phi_{n,g}$ is given by equation (7)

$$\Phi_{n,g}=(\frac{2d_g a_g}{N'_n})^{1/2}e^{-X/2}X^{\beta_{n,g}/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X) \qquad (56)$$

$$\hat{T}_1\Phi_{n,g}=(\frac{2d_g a_g}{N'_n})^{1/2}[-\frac{1}{2}X^{(\beta_{n,g}+2)/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)e^{-X/2}+\frac{\beta_{n,g}}{2}X^{\beta_{n,g}/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)e^{-X/2}+X^{(\beta_{n,g}+2)/2}\,{}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)e^{-X/2}] \qquad (57)$$

Evaluating, and noting the fact that:

$$\frac{d\,L^b_a(X)}{dX}=L^{b+1}_a(X)$$

$$\hat{T}_2\Phi_{n,g}=(\frac{2d_g a_g}{N'_n})^{1/2}e^{-X/2}[\frac{1}{4}X^{(\beta_{n,g}+4)}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)-\frac{\beta_{n,g}}{4}X^{(\beta_{n,g}+2)/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)-\frac{1}{2}X^{(\beta_{n,g}+4)/2}\,{}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)-\frac{\beta_{n,g}}{4}X^{(\beta_{n,g}+2)/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)$$
$$+\frac{\beta_{n,g}(\beta_{n,g-2})}{4}X^{\beta_{n,g}/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)+\frac{\beta_{n,g}}{2}X^{(\beta_{n,g}+2)/2}\,{}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)-\frac{1}{2}X^{(\beta_{n,g}+4)/2}\,{}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)$$
$$+\frac{\beta_{n,g}}{2}X^{(\beta_{n,g}+2)/2}\,{}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)+X^{(\beta_{n,g}+4)/2}\,{}_{s}L^{\beta_{n,g+2}}_{\beta_{n,g+n}}(X)] \qquad (58)$$

Therefore (55) becomes:

$$\hat{T}\Phi_{n,g}=E(\frac{2d_g a_g}{N'_n})^{1/2}\sum_{s=1}^{12}Z_s \qquad (59)$$

Where each of the twelve terms Zs is of the general form:

$$Zs=CX^p L^b_a(X)e^{-X/2} \qquad (60)$$

and Zs are listed explicitly in Table 2.
From potential energy operator (48):

$$\hat{V}e\,\Phi_{n,g}=AX^{2t}\Phi_{n,g}-BX^t\Phi_{n,g}$$

$$=(\frac{2d_g a_g}{N'_n})^{1/2}(AZ_{13}-BZ_{14}) \qquad (61)$$

$$Z_{13}=X^{(\beta_{n,g}+4t)/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)e^{-X/2} \qquad (62)$$

$$Z_{14}=X^{(\beta_{n,g}+2t)/2}\,{}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)e^{-X/2} \qquad (63)$$

The fourteen terms generated by $\hat{H}$, $\Phi_{n,g}$ are given by:

$$\hat{H}e\,\Phi_{n,g}=(\frac{2d_g a_g}{N'_n})^{\frac{1}{2}}[E\sum_{s=1}^{12}Z_s+AZ_{13}-BZ_{14}] \qquad (64)$$

Table 2. Kinetic Energy Operator Terms

$$Z_s\equiv e^{-X/2}X^{\beta_{n,g}/2}Z'_s$$

(1)	$Z'_1=$	$-\frac{1}{2}X$	${}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)$
(2)	$Z'_2=$	$\frac{\beta_{n,g}}{2}$	${}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)$
(3)	$Z'_3=$		${}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)$
(4)	$Z'_4=$	$\frac{1}{4}X^2$	${}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)$
(5)	$Z'_5=$	$-\frac{\beta_{n,g}}{4}X$	${}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)$
(6)	$Z'_6=$	$-\frac{1}{2}X^2$	${}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)$
(7)	$Z'_7=$	$-\frac{\beta_{n,g}}{4}X$	${}_{s}L^{\beta_{n,g}}_{\beta_{n,g+n}}(X)$
(8)	$Z'_8=$	$\frac{\beta_{n,g}}{2}X$	${}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)$
(9)	$Z'_9=$	$\frac{\beta_{n,g}}{2}X$	${}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)$
(10)	$Z'_{10}=$	$-\frac{1}{2}X^2$	${}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+n}}(X)$
(11)	$Z'_{11}=$	$\frac{\beta_{n,g}}{2}X$	${}_{s}L^{\beta_{n,g+1}}_{\beta_{n,g+1}}(X)$
(12)	$Z'_{12}=$	X^2	${}_{s}L^{\beta_{n,g+2}}_{\beta_{n,g+n}}(X)$

C. Matrix Element Evaluation and Recursion formulas. The Hamiltonian matrix elements are defined by equation (40)

$$H_{i,j}=\int \Phi^*_{i,g}\hat{H}e\,\Phi_{j,g}d\tau$$

Dropping the subscripts g and e where unambiguous, the Morse wavefunctions are given by:

$$\Phi_i=\left(\frac{2d_g a_g}{Ni'}\right)^{\frac{1}{2}} X^{\beta_i/2}\, {}_gL^{\beta_i}_{\beta_i+i}(X)\,e^{-X/2} \qquad (65)$$

$$\Phi_j=\left(\frac{2d_g a_g}{N_j'}\right)^{\frac{1}{2}} X^{\beta_j/2}\, {}_gL^{\beta_j}_{\beta_j+j}(X)\,e^{-X/2} \qquad (66)$$

From (50), $dr=\frac{1}{a_g}X^{-1}dX$

Table 3. Hamiltonian Matrix Elements (Morse potentials)

$H_{i,j}=\frac{2d_g}{(N_iN_j)^{\frac{1}{2}}}\sum_{s=1}^{14}F_s^{i,j}I_s^{i,j}\qquad M\equiv X^{(\beta_i+\beta_j)/2}e^{-X}$

S	$F_s^{i,j}$	$I_s^{i,j}$
1	$-\frac{E}{2}$	$\int M\, L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
2	$\frac{E\beta_j}{2}$	$\int MX^{-1} L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
3	E	$\int M\, L^{\beta_j+1}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
4	$\frac{E}{4}$	$\int MX\, L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
5	$-\frac{E\beta_j}{4}$	$\int M\, L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
6	$-\frac{E}{2}$	$\int MX\, L^{\beta_j+1}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
7	$-\frac{E\beta_j}{4}$	$\int M\, L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
8	$\frac{E\beta_j(\beta_j-2)}{4}$	$\int M\, L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
9	$\frac{E\beta_j}{2}$	$\int M\, L^{\beta_j+1}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
10	$-\frac{E}{2}$	$\int MX\, L^{\beta_j+1}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
11	$\frac{E\beta_j}{2}$	$\int M\, L^{\beta_j+1}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
12	E	$\int MX\, L^{\beta_j+2}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
13	A	$\int MX^{(2t-1)} L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$
14	B	$\int MX^{(t-1)} L^{\beta_j}_{\beta_j+j}(X)\, L^{\beta_i}_{\beta_i+i}(X)dX$

a) $\nu_e>\nu_g: A\equiv\frac{D_e}{(2d_g)^{2t}},\ B\equiv\frac{2D_e}{(2d_g)^t},\ E\equiv\frac{-a_g'^2\omega_g}{2}$

b) $\nu_e<\nu_g: A\equiv\frac{D_g}{(2d_e)^{2t}},\ B\equiv\frac{2D_g}{(2d_e)^t},\ E\equiv\frac{-a_g'^2\omega_e}{2}$

which implies that

$$\int\Phi_i(r)\,\hat{H}e\,\Phi_j(r)dr=-\frac{1}{a_g}\int X^{-1}\Phi_i(X)\hat{H}e\,\Phi_j(X)dX \qquad (67)$$

Thus the matrix elements, $H_{i,j}$ are given by:

$$H_{i,j}=\frac{-2d_g}{(Ni\ Nj)^{1/2}}\sum_{s=1}^{14}F_s^{i,j}\,I_s^{i,j} \qquad (68)$$

where the terms $F_s^{i,j}$ and $I_s^{i,j}$ are given in Table 3. In Table 3, $I_s^{i,j}$ is of the form:

$$I_s^{i,j}=\int\left(X^pe^{-X}L^{n_s}_{n_s+k_s}(X)\,L^{n'_s}_{n'_s+k'_s}(X)\right)dX \qquad (69)$$

which can be evaluated using Schroedinger's[5] paper

$$I_s^{i,j}=p!\,(n_s+k_s)!\,(n'_s+k'_s)!\sum_{\tau=0}^{\le k_s,k'_s}(-1)^{n_s+n'_s+k_s+k'_s+\tau}\binom{p-n_s}{k_s-\tau}\binom{p-n'_s}{k'_s-\tau}\binom{-p-1}{\tau} \qquad (70)$$

Equation (68) can be written as:

$$H_{i,j}=\sum_{s=1}^{14}F_s^{i,j}\,J_s^{i,j}\,G_s^{i,j} \qquad (71)$$

Table 4. Evaluation of Matrix Elements

$B_i=k\text{-}2i\text{-}1\quad B_j=k\text{-}2j\text{-}1$

S	P	n_s	k_s	n'_s	k'_s	$F_s^{i,j}$
1	k-i-j-1	k-2j-1	j	k-2i-1	i	$-\frac{E}{2}$
2	k-i-j-2	k-2j-1	j	k-2i-1	i	$\frac{E}{2}(k\text{-}2j\text{-}1)$
3*	k-i-j-1	k-2j	j-1	k-2i-1	i	E
4	k-i-j	k-2j-1	j	k-2i-1	i	$\frac{E}{4}$
5	k-i-j-1	k-2j-1	j	k-2i-1	i	$-\frac{E}{4}(k\text{-}2j\text{-}1)$
6*	k-i-j	k-2j	j-1	k-2i-1	i	$-\frac{E}{4}$
7	k-i-j-1	k-2j-1	j	k-2i-1	i	$-\frac{E}{4}(k\text{-}2j\text{-}1)$
8	k-i-j-2	k-2j-1	j	k-2i-1	i	$\frac{E}{4}(k\text{-}2j\text{-}1)(k\text{-}2j\text{-}3)$
9*	k-i-j-1	k-2j	j-1	k-2i-1	i	$\frac{E}{2}(k\text{-}2j\text{-}1)$
10*	k-i-j	k-2j	j-1	k-2i-1	i	$-\frac{E}{2}$
11*	k-i-j-1	k-2j	j-1	k-2i-1	i	$\frac{E}{2}(k\text{-}2j\text{-}1)$
12**	k-i-j	k-2j+1	j-2	k-2i-1	i	E
13	k-i-j-2+2t	k-2j-1	j	k-2i-1	i	A
14	k-i-j-2+t	k-2j-1	j	k-2i-1	i	$-B$

* $F_S^{i,j}, J_S^{i,j}, G_S^{i,j}=0$ if $j<1$. ** $F_S^{i,j}, J_S^{i,j}, G_S^{i,j}=0$ if $j<2$. E, A, B are defined previously.

Table 5. Recursion Relationships for all Diagonal Elements

$$J_1^{i,i} = \frac{i!\,(k-2i-1)}{(k-i-1)(k-i-2)\rightarrow(k-2i)}, \quad i>0$$

$$J_2^{i,i} = \frac{J_1^{i,i}}{(k-2i-1)}$$

$$J_4^{i,i} = J_1^{i,i}(k-2i)$$

$$J_{13}^{i,i}\,(t=2) = J_1^{i,i}(k-2i+2)(k-2i+1)(k-2i)$$

$$J_{13}^{i,i}\,(t=3) = J_1^{i,i}(k-2i+4)(k-2i+3)(k-2i+2)(k-2i+1)(k-2i)$$

$$J_{14}^{i,i}\,(t=3) = J_1^{i,i}(k-2i+1)(k-2i)$$

Table 6. Recursion Relationships for all off-diagonal Elements

$$J_1^{0,j} = \frac{[j!\,(k-1)(k-2j-1)]^{\frac{1}{2}}}{[(k-1)(k-2)\rightarrow(k-j)]^{\frac{1}{2}}}; \quad (i=0 \ \text{except} \ I_{121}=0)$$

$$J_1^{i,j} = \frac{[i!\,j!\,(k-2i-1)(k-2j-1)]^{\frac{1}{2}}}{[(k-j-1)\rightarrow(k-j-i)][(k-i-1)\rightarrow(k-j)]^{\frac{1}{2}}}; \quad (i>0)$$

$$J_2^{i,j} = \frac{J_1^{i,j}}{(k-i-j-1)}$$

$$J_4^{i,j} = J_1^{i,j}(k-i-j)$$

$$J_{13}^{i,j}(t=2) = J_1^{i,j}(k-i-j+2)(k-i-j+1)(k-i-j)$$

$$J_{13}^{i,j}(t=3) = J_1^{i,j}(k-i-j+4)(k-i-j+3)\rightarrow(k-i-j)$$

$$J_{14}^{i,j}(t=3) = J_1^{i,j}(k-i-j+1)(k-i-j)$$

where

$$J_S^{i,j} = \frac{2d_g}{(Ni\ Nj)^{\frac{1}{2}}} P!(n_s+k_s)!\,(n'_s+k'_s)!$$

$$G_S^{i,j} = \sum_{\tau=0}^{\leq k_S, k'_S} (-1)^{n_s+n'_s+k_s+k'_s+\tau} \binom{p-n_S}{k_S-\tau}\binom{p-n'_S}{k'_S-\tau}\binom{-p-1}{\tau}$$

The relevant values of p, n_s, k_s, n'_s, k'_s, and $F_s^{i,j}$ are given as functions of i and j for each integral in Table 4.

Consideration of Table 3 reveals that I_3, I_6, I_9, I_{10} and I_{11} must be zero if $j<1$. I_{12} must be zero if $j<2$. This can be shown to be true by the use of equation (15)[7]:

$${}_sL_a^b(y) = \frac{d^b}{dy^b}\left[e^y \frac{d^a}{dy^a}(y^a e^{-y})\right]$$

Clearly ${}_sL_a^b=0$ when b>a. This is the case in I_3, I_6, I_9, I_{10} and I_{11} when $j<1$ and I_{12} when $j<2$.

The following recursion relationships of the $J_s^{i,j}$ terms were calculated.

$$J_1^{i,j} = J_3^{i,j} = J_5^{i,j} = J_7^{i,j} = J_9^{i,j} = J_{11}^{i,j} = J_{14}^{i,j}\,(t=1) \qquad \text{(72-a)}$$

$$J_2^{i,j} = J_8^{i,j} \qquad \text{(72-b)}$$

$$J_4^{i,j} = J_6^{i,j} = J_{10}^{i,j} = J_{12}^{i,j>2} = J_{13}^{i,j}\,(t=1) = J_{14}^{i,j}\,(t=2) \qquad \text{(72-c)}$$

where the superscripts i, j designate all values of i and $j\geq0$ unless otherwise designated. The calculated recursion formulas for all diagonal elements except as designated are listed in Table 5 and off-diagonal elements in Table 6. Once the matrix elements are calculated by using these recursion relationships, they are placed into a column-packed upper triangular matrix to be diagonalized. The diagonalization then yields both the eigenvectors and the eigenvalues.

Conclusion

We have developed kinetic and potential operator for the Morse wavefunctions when the ground states frequencies and dissociation energies differ from those of excited states frequencies and dissociation energies. Also, we developed recursion formulas for vibrational matrix elements of Morse wavefunctions.

Examination of the literature revealed that there were no closed form evaluations of overlap integrals of Morse potential wavefunctions. However, molecules with relatively low dissociation energies are not approximated well by any of the harmonic and anharmonic potentials. We still need to more study for the refinements of some equations. From our results, the overlap integrals and spectral intensities of absorbance, fluorescence, Raman and CARS can be evaluated using Morse wavefunctions.

Appendix A. Important integrals for Morse Warefunctions. ($\nu_e>\nu_g$; $D_e\neq D_g$)

(a) $\int \phi^*_{0,g}\psi_{v,e}d\tau = \langle 0|v\rangle = \sum_m C_{vm}\langle 0|m\rangle$
$= C_{v0}\langle 0|0\rangle + C_{v1}\langle 0|1\rangle + C_{v2}\langle 0|2\rangle + \cdots$

(b) $\int \psi^*_{0,e}\phi_{i,g}d\tau = \langle 0|i\rangle = \sum_m C_{0m}\langle m|i\rangle$
$= C_{00}\langle 0|i\rangle + C_{01}\langle 1|i\rangle + C_{02}\langle 2|i\rangle + \cdots$

(c) $\int \psi^*_{v,e}\phi_{1,g}d\tau = \langle v|1\rangle = \sum_m C_{vm}\langle m|1\rangle$
$= C_{v0}\langle 0|1\rangle + C_{v1}\langle 1|1\rangle + C_{v2}\langle 2|1\rangle + \cdots$

(d) $\int \phi^*_{1,g}\psi_{v,e}d\tau = \langle 1|v\rangle = \sum_m C_{vm}\langle 1|m\rangle$
$= C_{v0}\langle 1|0\rangle + C_{v1}\langle 1|1\rangle + C_{v2}\langle 1|2\rangle + \cdots$

(e) $\int \psi^*_{v,e}\phi_{0,g}d\tau = \langle v|0\rangle = \sum_m C_{vm}\langle m|0\rangle$
$= C_{v0}\langle 0|0\rangle + C_{v1}\langle 1|0\rangle + C_{v2}\langle 2|0\rangle + \cdots$

(f) $\int \psi^*_{v,e}\phi_{2,g}d\tau = \langle v|2\rangle = \sum_m C_{vm}\langle m|2\rangle$
$= C_{v0}\langle 0|2\rangle + C_{v1}\langle 1|2\rangle + C_{v2}\langle 2|2\rangle + \cdots$

(g) $\int \phi^*_{2,g}\psi_{v,e}d\tau = \langle 2|v\rangle = \sum_m C_{vm}\langle 2|m\rangle$
$= C_{v0}\langle 2|0\rangle + C_{v1}\langle 2|1\rangle + C_{v2}\langle 2|2\rangle + \cdots$

Appendix B. Important integrals for Morse Wavefunctions. ($\nu_e<\nu_g$; $D_e\neq D_g$)

(a) $\int \phi^*_{0,g}\psi_{v,e}d\tau = \langle 0|v\rangle = \sum_t C_{0t}\langle t|v\rangle$
$= C_{00}\langle 0|v\rangle + C_{01}\langle 1|v\rangle + C_{02}\langle 2|v\rangle + \cdots$

(b) $\int \psi^*_{0,e}\phi_{i,g}d\tau = \langle 0|i\rangle = \sum_t C_{it}\langle 0|t\rangle$
$= C_{i0}\langle 0|0\rangle + C_{i1}\langle 0|1\rangle + C_{i2}\langle 0|2\rangle + \cdots$

(c) $\int \psi^*_{v,e}\phi_{1,g}d\tau = \langle v|1\rangle = \sum_t C_{1t}\langle v|t\rangle$
$= C_{10}\langle v|0\rangle + C_{11}\langle v|1\rangle + C_{12}\langle v|2\rangle + \cdots$

(d) $\int \phi^*_{1,g}\psi_{v,e}d\tau = \langle 1|v\rangle = \sum_t C_{1t}\langle 1|v\rangle$
$= C_{10}\langle 0|v\rangle + C_{11}\langle 1|v\rangle + C_{12}\langle 2|v\rangle + \cdots$

(e) $\int \psi^*_{v,e}\phi_{0,g}d\tau = \langle v|0\rangle = \sum_t C_{0t}\langle v|t\rangle$
$= C_{00}\langle v|0\rangle + C_{01}\langle v|1\rangle + C_{02}\langle v|2\rangle + \cdots$

$$\text{(f)} \int \psi^*_{v,e}\phi_{2,g} d\tau = \langle v|2\rangle = \sum_t C_{2t}\langle v|t\rangle = C_{20}\langle v|0\rangle + C_{21}\langle v|1\rangle + C_{22}\langle v|2\rangle + \cdots$$

$$\text{(g)} \int \phi^*_{2,g}\psi_{v,e} d\tau = \langle 2|v\rangle = \sum_t C_{2t}\langle t|v\rangle = C_{20}\langle 0|v\rangle + C_{21}\langle 1|v\rangle + C_{22}\langle 2|v\rangle + \cdots$$

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Lead Tolerance of Noble Metal Catalysts for CO Oxidation

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Lead tolerance of Pt/Al_2O_3 catalysts was evaluated for CO oxidation depending on the properties of the alumina supports and base metals added as promoter. Among the four different alumina supports, the support with a large macropore volume (0.45cc/g) and 5% Ce has shown the best resistence to lead poisoning. Most of the base metals added to the Pt-catalysts were found to be ineffective for improving lead resistence, but boron has shown an excellent lead tolerence, although it decreases the initial catalytic activity.

Introduction

The major cause of catalyst deactivation in the automobile systems using leaded gasoline is poisoning by lead. Although the lead deactivation has recently been reviewed by several authors,[1-4] its detailed mechanism was not completely understood. Some of the important aspects of lead poisoning known by experiments are that among the single component metal catalysts, Pt-catalyst is most resistant to lead poisoning and a considerable fraction (10–30%) of the lead in the fuel consumed is deposited on the catalyst as lead sulfate or phosphate in major. Such a coating of lead salts on the catalyst surface cause poor mass transfer properties[3] resulting in decrease of its activity. Furthermore, experiments have shown only a small changes in the macropore volume of the support Al_2O_3 while a remarkable decrease in the micropore volume was observed.[5]

In this paper we present the results of the attempts to prepare lead-tolerant catalysts for CO oxidation by impregnating platinum into modified γ-Al_2O_3 supports with different properties and by promoting the Pt-catalyst using various base-metals.

Experimental

Preparation of Pt-catalysts supported on γ-Al_2O_3. Pt-impregnated catalysts were prepared using four different kinds of γ-Al_2O_3 pellets of 2–8mm in diameter obtained from Rhone-Poulenc. Their characterestic properties are shown in Table 1.

In order to load platinum an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ with pH adjusted to 2.5 ± 0.5 using HCl solution was impregnated on the alumina supports. An exact amount of the Pt-solution containing 0.2% Pt of the alumina support was taken into a round-bottom flask together with the dried alumina pellets and then evaporated to dryness in a rotary evaporator at 85°C. The catalyst was dried at 150°C in oven and then calcined for 4 hours at 550°C. The catalyst was then reduced under hydrogen atmosphere for 2 hours at 550°C before use.