Linear and derivative nuclear operators in single-$\hbar\omega_0$, multiple-coordinate models of luminescence centers

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The known nuclear factors for the rates of transitions driven by the z and $\partial/\partial z$ operators in one coordinate are generalized to two and then to any number of coordinates. In the notation $O_+ = z$, $O_- = \partial/\partial z$, the nuclear factors $W_{p,O_\pm}$ for one and $M_{p,O_\pm}$ for multiple coordinates are related by $M_{p,O_\pm} = (1-\gamma)\, W_{p,O_\pm} + \gamma L_p$. The functions $W_{p,O_\pm}$ and L_p are combinations of Huang-Rhys-Pekar $W_p(S, \langle m\rangle)$ functions. The parameter γ lies between 0 and 1. The factor $M_{p,\partial/\partial z}$ agrees with factors derived for the $\partial/\partial z$ operator in 10^{22} coordinates by Huang and Rhys and by Perlin. The largest differences between $W_{p,O_\pm}$ and $M_{p,O_\pm}$ are in the region p near S for S large.

I. INTRODUCTION

This paper describes the nuclear factor in the transition rate between two electronic states for single-$\hbar\omega_0$ models, namely, models in which all nuclear coordinates are independent and have the same phonon energy $\hbar\omega_0$.

Nuclear factors in single-$\hbar\omega_0$ models are expressible in Huang-Rhys-Pekar (HRP)[1-3] $W_p(S, \langle m\rangle)$ functions. These functions are defined as the normalized ($\sum_{p=-\infty}^{+\infty} W_p = 1$) solution of the three-term recursion formula

$$S\langle m\rangle W_{p+1} + pW_p - S\langle 1+m\rangle W_{p-1} = 0 \qquad (1)$$

and are given by

$$W_p(S, \langle m\rangle) = \exp(-S\langle 1+2m\rangle) \times \sum_{j=j_0}^{\infty} \frac{(S\langle m\rangle)^j (S\langle 1+m\rangle)^{p+j}}{j!(p+j)!} , \qquad (2)$$

where j_0 is the larger of 0 and $-p$, as may be verified by entering Eq. (2) in Eq. (1) and in the normalization condition. In nuclear factors, the index p is the number of phonons generated in the transition, and the arguments S and $\langle m\rangle$ are, respectively, the HRP measure of Franck-Condon offset and the Planck average-thermal-occupancy measure of the temperature.

The following W_p-function combinations are useful in stating the nuclear factors compactly:

$$L_p = \tfrac{1}{2}(\langle 1+m\rangle W_{p-1} + \langle m\rangle W_{p+1}) ,$$

$$W_{p,z} = \frac{1}{2S}(p-S)^2 W_p ,$$

$$W_{p,\partial/\partial z} = W_{p,z} - 2S\langle 1+m\rangle \langle m\rangle \times (W_{p-1} - 2W_p + W_{p+1}) . \qquad (3)$$

The rate of the transition in which p phonons are generated is, in N coordinates,

$$R_p = \sum_{n,m} (1-r)^N r^{m_1+m_2+\cdots+m_N} |\langle u_{n_1} u_{n_2} \cdots u_{n_N} | O | v_{m_1} v_{m_2} \cdots v_{m_N}\rangle|^2 , \qquad (4)$$

where O is the nuclear operator that results following integration over the electronic coordinates. In Eq. (4), the v_m and u_n are the initial and final vibrational wave functions, the n,m indices are constrained to satisfy $\sum_i (n_i - m_i) = p$, and r is the Boltzmann factor $\exp(-\hbar\omega_0/kT)$ related to $\langle m\rangle$ by

$$\langle m\rangle \equiv \sum_0^{\infty} m(1-r)r^m = \frac{r}{1-r} = [\exp(\hbar\omega_0/kT) - 1]^{-1} \qquad (5)$$

For the Condon-approximation operator $O = A = \text{constant}$, R_p in Eq. (4) is, in any number of coordinates, $A^2 W_p$, where A^2 and W_p are the transition electronic and nuclear factors, respectively. W_p is the HRP W_p function for the offset $S = \sum_i S_i$, where S_i is the offset between the initial and the final states in the ith coordinate. This nuclear factor has been derived for one coordinate,[4–12] for the HRP lattice model (which we arbitrarily characterize as $\sim 10^{22}$ coordinates, the number of modes in a 1-cm^3 crystal),[1–5,7,13,14] and for an arbitrary number of coordinates.[5,9,15]

For the linear (z) and derivative ($\partial/\partial z$) operators in one coordinate, R_p in Eq. (4) is $A^2 W_{p,z}$ and $A^2 W_{p,\partial/\partial z}$, respectively, where A^2 is the electronic factor and the nuclear factors $W_{p,z}$ and $W_{p,\partial/\partial z}$ are the W_p combinations in Eq. (3). The nuclear factor for z was derived by Wagner[9] and Koide[10] and the factors for z and $\partial/\partial z$ by Struck and Fonger.[16]

In multiple coordinates $N \geq 2$, the linear and derivative operators are $O_z = \sum_i A_i z_i$ and $O_{\partial/\partial z} = \sum_i A_i \partial/\partial z_i$, and R_p in Eq. (4) is

$$\begin{aligned} R_{p,z} &= A^2[(1-\gamma) W_{p,z} + \gamma L_p] \equiv A^2 M_{p,z} , \\ R_{p,\partial/\partial z} &= A^2[(1-\gamma) W_{p,\partial/\partial z} + \gamma L_p] \\ &\equiv A^2 M_{p,\partial/\partial z} , \end{aligned} \tag{6}$$

where the nuclear factors $M_{p,z}$ and $M_{p,\partial/\partial z}$ use the W_p-function combinations $L_p, W_{p,z}$, and $W_{p,\partial/\partial z}$ in Eq. (3), and the electronic factor A^2 and the parameters S and γ are given by

$$\begin{aligned} A^2 &= \sum_{i=1}^{N} |A_i|^2 , \quad S = \sum_{i=1}^{N} S_i , \\ \gamma &= 1 - (A^2 S)^{-1} \left| \sum_{i=1}^{N} A_i S_i^{1/2} \right|^2 . \end{aligned} \tag{7}$$

The constant γ needed for multiple coordinates lies between 0 and +1. For one coordinate, $\gamma = 0$, and $M_{p,z}$ and $M_{p,\partial/\partial z}$ in Eq. (6) reduce to the one-coordinate z and $\partial/\partial z$ nuclear factors $W_{p,z}$ and $W_{p,\partial/\partial z}$, respectively.

The multiple-coordinate rates (6) are derived for any $N \geq 2$ in this paper. $R_{p,\partial/\partial z}$ in Eq. (6) had been derived for 10^{22} coordinates by Huang and Rhys[1] and Perlin.[13,14] The present work bridges the gap between the one-coordinate formulas and the Huang-Rhys-Perlin formulas for $\partial/\partial z$ in 10^{22} coordinates.

II. $M_{p,z}$ AND $M_{p,\partial/\partial z}$ FORMULAS

Formulas (6) for $M_{p,z}$ and $M_{p,\partial/\partial z}$ will be derived first for two coordinates. The notation $O_{i+} = z_i$, $O_{i-} = \partial/\partial z_i$ will be used. This notation reflects well-known formulas for the linear and derivative matrix elements and allows these matrix elements to be written in a single equation,

$$\begin{aligned} \langle u_n | O_\pm | v_m \rangle &= (\tfrac{1}{2} m)^{1/2} \langle u_n | v_{m-1} \rangle \\ &\pm [\tfrac{1}{2}(m+1)]^{1/2} \langle u_n | v_{m+1} \rangle . \end{aligned} \tag{8}$$

See Sec. II of Ref. 16 for a sketch of the derivation of Eq. (8). Both $M_{p,O_\pm}$ formulas can now be obtained in a single development

$$\begin{aligned} A^2 M_{p,O_\pm} &= \sum_{n_1 m_1 n_2 m_2} | \langle u_{n_1} u_{n_2} | A_1 O_{1\pm} + A_2 O_{2\pm} | v_{m_1} v_{m_2} \rangle |^2 (1-r)^2 r^{m_1+m_2} \\ &= \sum_{p_1 p_2 m_1 m_2} [\, |A_1|^2 \langle u_{p_1+m_1} | O_{1\pm} | v_{m_1} \rangle^2 \langle u_{p_2+m_2} | v_{m_2} \rangle^2 + |A_2|^2 \langle u_{p_1+m_1} | v_{m_1} \rangle^2 \langle u_{p_2+m_2} | O_{2\pm} | v_{m_2} \rangle^2 \\ &\quad + (A_1 A_2^* + A_2 A_1^*) \langle u_{p_1+m_1} | v_{m_1} \rangle \langle u_{p_1+m_1} | O_{1\pm} | v_{m_1} \rangle \langle u_{p_2+m_2} | v_{m_2} \rangle \\ &\quad \times \langle u_{p_2+m_2} | O_{2\pm} | v_{m_2} \rangle] (1-r)^2 r^{m_1+m_2} \\ &= \sum_{p_1} [\, |A_1|^2 W_{p_1, O_{1\pm}} W_{p_2} + |A_2|^2 W_{p_1} W_{p_2, O_{2\pm}} + (A_1 A_2^* + A_2 A_1^*) X_{p_1, O_{1\pm}} X_{p_2, O_{2\pm}}] . \end{aligned} \tag{9}$$

In the last form of Eq. (9), the W's are single-coordinate nuclear factors described in Sec. I, and the X's in the cross term are the single-coordinate quantities

$$\begin{aligned} X_{p,O_\pm} &\equiv \sum_{m=m_0}^{+\infty} \langle u_{p+m} | v_m \rangle \langle u_{p+m} | O_\pm | v_m \rangle (1-r) r^m \\ &= (\tfrac{1}{2} S)^{1/2} [\, \langle m \rangle (W_p - W_{p+1}) \pm \langle 1+m \rangle (W_{p-1} - W_p)] , \end{aligned} \tag{10}$$

where m_0 is the larger of 0 and $-p$. This evaluation of $X_{p,O\pm}$ is derived in Appendix A using Eq. (8) and the Manneback recursion formulas[12,17] for the overlap integrals $\langle u_n | v_m \rangle$.

In the last form of Eq. (9) and in the equations below, the W's and X's are written without their arguments $S, \langle m \rangle$. It should be understood that, if the W or X subscript is p_1 (or p_2), the arguments are $S_1, \langle m \rangle$ (or $S_2, \langle m \rangle$). In the first form of Eq. (9), n_1, n_2, m_1, m_2 are constrained by $(n_1 - m_1) + (n_2 - m_2) = p$. In the last two forms of Eq. (9) and in the equations below, p_1 is summed from $-\infty$ to $+\infty$, and p_1, p_2 are constrained by $p_1 + p_2 = p$. In the second form of Eq. (9), m_1 is summed from $m_{1,0}$ to ∞, where $m_{1,0}$ is the larger of 0 and $-p_1$; and m_2 similarly.

The formulas for $W_{p,O\pm}$ in Eqs. (3) are the simplest for these nuclear factors but are not the most convenient for summing over p_1 in Eq. (9). In Appendix B, it is shown through the W_p recursion formula (1) that $W_{p,O\pm}$ can be written

$$W_{p,O\pm} = L_p + S \sum_{i=-2}^{+2} \alpha_{i,O\pm} W_{p+i} , \tag{11}$$

where L_p is the W_p combination in Eq. (3) and the $\alpha_{i,O\pm}$, given in Appendix B, are "temperature coefficients" depending only on $\langle m \rangle$.

With $W_{p,O\pm}$ given by Eq. (11) and $X_{p,O\pm}$ by Eq. (10), all terms in Eq. (9) are of the form $K W_{p_1+i} W_{p_2+j}$, where K is independent of p_1, p_2. These terms can be summed over p_1 through application of the reproductive formula for HRP W_p functions, namely,[9,15]

$$\sum_{p_1=-\infty}^{+\infty} W_{p_1}(S_1, \langle m \rangle)\, W_{p_2}(S_2, \langle m \rangle) = W_p(S_1 + S_2, \langle m \rangle) , \tag{12}$$

where $p_1 + p_2 = p$. Such an application gives

$$\sum_{p_1=-\infty}^{+\infty} K W_{p_1+i} W_{p_2+j} = K W_{p+i+j}(S_1 + S_2, \langle m \rangle) , \tag{13}$$

where W_{p+i+j} has for its S argument the sum of S_1 and S_2.

Making use of Eq. (13), expression (9) becomes

$$\begin{aligned} A^2 M_{p,O\pm} = {} & |A_1|^2 \left(L_p + S_1 \sum_{i=-2}^{+2} \alpha_{i,O\pm} W_{p+i} \right) \\ & + |A_2|^2 \left(L_p + S_2 \sum_{i=-2}^{+2} \alpha_{i,O\pm} W_{p+i} \right) \\ & + (A_1 A_2^* + A_2 A_1^*) \\ & \times (S_1 S_2)^{1/2} \sum_{i=-2}^{+2} \alpha_{i,O\pm} W_{p+i} . \end{aligned} \tag{14}$$

In Eq. (14), the arguments of all W_p's, including those underlying L_p, are $S, \langle m \rangle$, where $S = S_1 + S_2$. The $|A_1|^2$ and $|A_2|^2$ terms in Eq. (14) are evident from Eq. (11), but the $A_1 A_2^* + A_2 A_1^*$ cross term is not evident from Eq. (10). The computation of this cross term is given in Appendix C.

Formula (14) can now be developed as

$$\begin{aligned} A^2 M_{p,O\pm} &= [|A_1|^2 S_1 + |A_2|^2 S_2 + (A_1 A_2^* + A_2 A_1^*)(S_1 S_2)^{1/2}] \left(\sum_{i=-2}^{+2} \alpha_{i,O\pm} W_{p+i} \right) + (|A_1|^2 + |A_2|^2) L_p \\ &= |A_1 S_1^{1/2} + A_2 S_2^{1/2}|^2 S^{-1} (W_{p,O\pm} - L_p) + (|A_1|^2 + |A_2|^2) L_p = A^2 [(1-\gamma) W_{p,O\pm} + \gamma L_p] , \end{aligned} \tag{15}$$

where A^2, S, and γ are given as in Eqs. (7) for $N = 2$.

The $M_{p,O\pm}$ formulas for three, four, or more coordinates are obtained similarly. For example, for three coordinates, terms of the form $|A_1|^2 W_{p_1,O_1\pm} W_{p_2} W_{p_3}$ and

$$(A_1 A_2^* + A_2 A_1^*) X_{p_1,O_1\pm} X_{p_2,O_2\pm} W_{p_3}$$

are obtained; and p_1, p_2 are summed from $-\infty$ to $+\infty$ with p_1, p_2, p_3 constrained by $p_1 + p_2 + p_3 = p$. Using Eq. (11) for $W_{p,O\pm}$ and Eq. (10) for $X_{p,O\pm}$, these terms are summed through the HRP W_p reproductive formula in three coordinates,

$$\sum_{p_1,p_2=-\infty}^{+\infty} W_{p_1}(S_1, \langle m \rangle)\, W_{p_2}(S_2, \langle m \rangle)\, W_{p_3}(S_3, \langle m \rangle) = W_p(S_1 + S_2 + S_3, \langle m \rangle) , \tag{16}$$

where $p_1 + p_2 + p_3 = p$; and Eqs. (6) for $M_{p,O\pm}$ again result, where A^2, S, and γ are given as in Eq. (7) for $N = 3$.

The parameter γ in $M_{p,O_\pm}$ is a new parameter not in the one-coordinate model. Its value lies between 0 and +1. To show this, one adds to the square $|\sum_i A_i S_i^{1/2}|^2$ in γ in Eq. (7) all possible squares of the form $|A_i S_j^{1/2} - A_j S_i^{1/2}|^2$. This addition gives

$$\Omega \equiv |\sum_{i=1}^{N} A_i S_i^{1/2}|^2 + \sum_{i,j>i}^{N} |A_i S_j^{1/2} - A_j S_i^{1/2}|^2 = \left(\sum_{i=1}^{N} |A_i|^2\right)\left(\sum_{i=1}^{N} S_i\right) = A^2 S \ . \tag{17}$$

Since all the added terms are non-negative, it follows that $|\sum_i A_i S_i^{1/2}|^2$ lies between 0 and A^2S and therefore that, as asserted, γ in Eq. (7) lies between 0 and +1.

The parameter γ is a measure of the unevenness of the A_i and $S_i^{1/2}$ for the different coordinates. If all A_i and $S_i^{1/2}$ are the same or if all $A_i = \alpha S_i^{1/2}$ where α is a constant, it follows from Eq. (7) that $|\sum_i A_i S_i^{1/2}|^2 = A^2 S$ and $\gamma = 0$. Significant differences among the $A_i, S_i^{1/2}$ values are needed to make γ appreciable. For example, if N is even, all the A_i equal A_0, and half the $S_i^{1/2}$ equal $S_0^{1/2}$ and half equal $2S_0^{1/2}$, then

$$|\sum_i A_i S_i^{1/2}|^2 = \tfrac{9}{4} N^2 |A_0|^2 S_0 \ ,$$

$$A^2 S = \tfrac{5}{2} N^2 |A_0|^2 S_0 \ ,$$

and $\gamma = 0.1$. The same result obtains if all the $S_i^{1/2}$ equal $S_0^{1/2}$ and half the A_i equal A_0 and half equal $2A_0$. The root $S_i^{1/2}$ is a signed quantity,[12] and A_i can be complex. Though $\sum_i A_i S_i^{1/2}$ might therefore sum to zero and γ then be 1, we have no particular expectation that γ values will lie close to 1.

The transition rate for the $\partial/\partial z$ operator had been calculated for 10^{22} coordinates (the HRP lattice model) by Huang and Rhys[1] and Perlin.[13,14] Huang and Rhys gave as their rate

$$R_{p,\partial/\partial z} = \frac{h^2}{\omega_l}\Big\{ Z^2 L_p + |Y|^2[(\tfrac{1}{2} + \langle m\rangle)^2 + \tfrac{1}{2}\langle 1+m\rangle\langle m\rangle] W_p - |Y|^2\langle 2m+1\rangle L_p + \tfrac{1}{4}|Y|^2(\langle m\rangle^2 W_{p+2} + \langle 1+m\rangle^2 W_{p-2})\Big\} . \tag{18}$$

This formula is $R_{p,\partial/\partial z}$ in Eq. (6) with $W_{p,\partial/\partial z}$ in Eq. (6) written in the five-W_p form (11) and with A^2 and γ in the notation

$$A^2 = h^2 Z^2/\omega_l, \quad \gamma = 1 - |Y|^2/2Z^2 S \ .$$

Perlin gave as his rate

$$R_{p,\partial/\partial z} = \frac{\pi\omega}{(E_u - E_g)^2} \exp(-\tfrac{1}{2} a \coth\beta + p\beta)\left\{ \frac{1+2\cosh^2\beta}{4\sinh^2\beta} |b_{ug}|^2 I_p(x) + \frac{c_{ug} - |b_{ug}|^2\coth\beta}{2\sinh\beta} \times [I_{p-1}(x) + I_{p+1}(x)] + \frac{|b_{ug}|^2}{8\sinh^2\beta}[I_{p-2}(x) + I_{p+2}(x)]\right\} , \tag{19}$$

where $\beta = \hbar\omega_0/2kT$ and $x = a/2\sinh\beta$. This formula too is $R_{p,\partial/\partial z}$ in Eq. (6) with $W_{p,\partial/\partial z}$ in Eq. (6) in the five-W_p form (11), with the W_p functions expressed in $I_p(x)$ Bessel functions as

$$\exp(-\tfrac{1}{2} a\coth\beta + p\beta) I_p(a/2\sinh\beta) \ ,$$

and with the notation

$$S = \tfrac{1}{2} a, \quad A^2 = \frac{2\pi\omega c_{ug}}{(E_u - E_g)^2} \ , \quad \gamma = 1 - \frac{|b_{ug}|^2}{c_{ug} a} \ .$$

Thus, the $M_{p,\partial/\partial z}$ formula derived here for $N \geq 2$ coordinates agrees with the Huang-Rhys and Perlin $\partial/\partial z$ formulas in 10^{22} coordinates. Not having the one-coordinate weight $W_{p,\partial/\partial z}$, Huang and Rhys were not motivated to relate the one- and multiple-coordinate weights $W_{p,\partial/\partial z}$ and $M_{p,\partial/\partial z}$ in the simple manner Eq. (6) here. Also, they did not appreciate that the five-W_p combination (18) can be contracted via the W_p recursion formula to the more transparent three-W_p form (6) with Eq. (3).

Miyakawa and Dexter[18] have also calculated the $\partial/\partial z$-operator rate in multiple coordinates. They used a more complicated model with a spectrum of phonon energies $\hbar\omega$ but, in the end, particularized to a single phonon energy $\hbar\omega_0$. Thus, their final nuclear factor should have been the multiple-coordinate weight $M_{p,\partial/\partial z}$. It was not.

We are uncertain how to read the temperature dependence of their weight because the Miyakawa and Dexter coupling parameter g is referred to in text as a constant yet seems to be defined in their Eq. (3.16) as increasing with temperature as our quantity $S\langle 2m+1\rangle$. At 0 K, their g is certainly our S, and

their formula for $M_{p,\partial/\partial z}$, offered for S small, is [their Eq. (5.6)] $(1-p/S)^2 S^p/p!$. At 0 K, W_p reduces to the Poisson distribution $e^{-S}S^p/p!$, and the exact $M_{p,\partial/\partial z}$ weight obtained here and by Huang and Rhys and Perlin is

$$M_{p,\partial/\partial z}(0\text{ K}) = \frac{1}{2S}[(1-\gamma)(p-S)^2 + \gamma p]e^{-S}S^p/p!\ . \quad (20)$$

The Miyakawa and Dexter expression is a multiple of the 0-K one-coordinate weight $W_{p,\partial/\partial z}$ [obtained by taking $\gamma = 0$ in Eq. (20)]. We conclude that their approximations led them to miss the additional parameter γ in Eq. (20) required for multiple coordinates.

III. SUMS OVER THE p DISTRIBUTIONS AND THE LIMIT $S \to 0$

The temperature coefficients $\alpha_{i,O_\pm}$ in Eq. (11) and in Appendix B have the property

$$\sum_{i=-2}^{+2} \alpha_{i,z} = \sum_{i=-2}^{+2} \alpha_{i,\partial/\partial z} = 0\ . \quad (21)$$

This property leads to simple sums over p for the various distributions. Starting from the HRP W_p-function normalization $\sum_p W_p = 1$ and making use of Eq. (11) and L_p in Eq. (3), one has

$$\sum_{p=-\infty}^{+\infty} W_{p,O_\pm} = \sum_{p=-\infty}^{+\infty}\left[L_p + S\sum_{i=-2}^{+2}\alpha_{i,O_\pm} W_{p+i}\right] = \sum_{p=-\infty}^{+\infty} L_p = \tfrac{1}{2}\langle 1+2m\rangle\ . \quad (22)$$

It then follows that

$$M_{p,O_\pm} = (1-\gamma)\, W_{p,O_\pm} + \gamma L_p$$

has the same sum $\frac{1}{2}\langle 1+2m\rangle$ as $W_{p,O_\pm}$ and L_p. These sums are useful for checking numerically computed p distributions.

For $S \to 0$, the distributions W_p, L_p, $W_{p,O_\pm}$, and $M_{p,O_\pm}$ have limiting behaviors which are readily derived. For $S \to 0$, the offset u_n and v_m wave functions coalesce into a single orthonormal set u_n, and their overlap integrals $\langle u_n | v_m\rangle$ approach $\langle u_n | u_m\rangle = \delta_{nm}$. Thus, for the weight W_p for the operator 1,

$$W_p = \sum_{m=m_0}^{\infty}(1-r)r^m\langle u_{p+m}|v_m\rangle^2 \to \sum_{m=m_0}^{\infty}(1-r)r^m\delta_{p,0} = \delta_{p,0}\ . \quad (23)$$

For the function L_p, we have

$$L_p = \tfrac{1}{2}(\langle 1+m\rangle W_{p-1} + \langle m\rangle W_{p+1}) \to \tfrac{1}{2}(\langle 1+m\rangle\delta_{p,+1} + \langle m\rangle\delta_{p,-1})\ . \quad (24)$$

For the weights $W_{p,O_\pm}$ for the operators $O_\pm$ in one coordinate, we have, from Eqs. (4), (8), and (5),

$$W_{p,O_\pm} = \sum_{m=m_0}^{\infty}(1-r)r^m\{(\tfrac{1}{2}m)^{1/2}\langle u_{p+m}|v_{m-1}\rangle \pm [\tfrac{1}{2}(m+1)]^{1/2}\langle u_{p+m}|v_{m+1}\rangle\}^2 \to \sum_{m=m_0}^{\infty}(1-r)r^m[\tfrac{1}{2}m\,\delta_{p,-1} + \tfrac{1}{2}(m+1)\delta_{p,+1}] = \tfrac{1}{2}(\langle m\rangle\delta_{p,-1} + \langle 1+m\rangle\delta_{p,+1})\ . \quad (25)$$

It then follows that

$$M_{p,O_\pm} = (1-\gamma)\, W_{p,O_\pm} + \gamma L_p$$

has the same $S \to 0$ limit

$$\tfrac{1}{2}(\langle 1+m\rangle\delta_{p,+1} + \langle m\rangle\delta_{p,-1})$$

as $W_{p,O_\pm}$ and L_p. Thus, $W_{p,O_\pm}$ and $M_{p,O_\pm}$ are the same for $S \to 0$. The sums of the limiting distributions are $\frac{1}{2}\langle 1+2m\rangle$ in agreement with the sums (22).

Rebane's book[19] gives a qualitative picture of these limits as selection rules, namely, as the rules $p = 0$ for the operator 1 and $p = \pm 1$ for the operator $0_+ = z$. For $4f \to 4f$ and $3d \to 3d$ narrow-line transitions, the offsets S are in the range 0.05–0.3 and are not small enough for these limiting distributions to be realized. See the numerical analyses in Sec. IV.

IV. DIFFERENCES BETWEEN ONE- AND MULTIPLE-COORDINATE p DISTRIBUTIONS

The nonradiative rate and its temperature dependence can be inferred from the thermal quenching of luminescence. In Refs. 16 and 20, the four types of thermal quenching [bottom crossover, outside crossover, small-offset multiphonon emission, and inside (or tunneling) crossover] were analyzed in one coordinate for nonradiative transitions driven by the operators 1, z, or $\partial/\partial z$. These examples are now reconsidered for the z and $\partial/\partial z$ operators in multiple coordinates, where the results might be different.

For the operators $O_\pm$ in multiple coordinates, the nuclear factors are $M_{p,O_\pm} = (1-\gamma)\, W_{p,O_\pm} + \gamma L_p$, where $0 \leq \gamma \leq 1$. Thus, to compare multiple-coordinate $M_{p,O_\pm}$ with one-coordinate $W_{p,O_\pm}$, it is necessary only

to compare $W_{p,O\pm}$ and L_p. The values of $W_{p,O\pm}$ and L_p appropriate to the four quenching examples are given in Table I. Values renormalized to unity at 0 K are also shown.

In the first three examples, L_p is closely a multiple of either $W_{p,z}$ or $W_{p,\partial/\partial z}$. In the last three examples, L_p is small compared to either $W_{p,z}$ or $W_{p,\partial/\partial z}$. Thus, $M_{p,O\pm}$ can hardly differ from $W_{p,O\pm}$, because $W_{p,O\pm}$ and L_p are so similar, or because L_p is small, or both. These four examples representative of thermal quenching are therefore not useful for distinguishing between $W_{p,O\pm}$ and $M_{p,O\pm}$.

From the sums (22) where $\sum_p W_{p,O\pm} = \sum_p L_p$, one recognizes that there are p values for which L_p is not small compared to $W_{p,O\pm}$. In fact, L_p is greater than or comparable to $W_{p,z} = [(p-S)^2/2S]\,W_p$ for p near S and small compared to $W_{p,z}$ for p far from S. We therefore address the region p near S (near the maximum in the W_p distribution) where $W_{p,O\pm}$ can be small but L_p is large, and, therefore, $M_{p,O\pm}$ can differ from $W_{p,O\pm}$. This region was not investigated in the Table I quenching examples.

The distributions W_p, L_p, and $W_{p,O\pm}$ are plotted in Fig. 1 for the case of large offset ($S=9$). W_p and L_p are similar broad-band distributions with a single maximum near $p=S=9$. Their band shape is similar to the familiar Gaussian band of broad-band luminescence. $W_{p,z}$ at all temperatures and $W_{p,\partial/\partial z}$ at low temperature have a double maximum with a center node at $p=S=9$. This node is due to the $[(p-S)^2/2S]\,W_p$ term common to both $W_{p,z}$ and $W_{p,\partial/\partial z}$; see Eqs. (3). At high temperatures, $W_{p,\partial/\partial z}$

TABLE I. Examples of the thermal quenching of luminescence taken from Refs. 16 and 20. The nonradiative nuclear factors are $W_{p,O\pm}$ in the single-configurational-coordinate model, $(1-\gamma)\,W_{p,O\pm}+\gamma L_p$ in the multiple-coordinate model, with $0\leq\gamma\leq 1$.

Bottom crossover, $S=6.25$, $p=14$.

$kT/\hbar\omega_0$	$\langle m\rangle$	$10^2 W_{p,z}$		$10^2 W_{p,\partial/\partial z}$		$10^2 L_p$	
0	0	1.48	1	1.48	1	0.34	1
0.45	0.122	2.29	1.55	1.88	1.27	0.56	1.62
0.65	0.273	3.45	2.34	2.29	1.56	0.90	2.63
0.95	0.536	5.58	3.78	2.85	1.93	1.66	4.81

Outside crossover, $S=6.25$, $p=25$.

$kT/\hbar\omega_0$	$\langle m\rangle$	$10^6 W_{p,z}$		$10^6 W_{p,\partial/\partial z}$		$10^6 L_p$	
0	0	0.276	1	0.276	1	0.020	1
0.45	0.122	1.30	4.72	1.16	4.19	0.09	4.80
0.65	0.273	6.40	23.2	4.91	17.8	0.47	24.1
0.95	0.536	52.1	189.0	31.5	114.0	4.1	207.0

Small-offset multiphonon emission, $S=0.09$, $p=6$.

$kT/\hbar\omega_0$	$\langle m\rangle$	$10^7 W_{p,z}$		$10^7 W_{p,\partial/\partial z}$		$10^7 L_p$	
0	0	1.31	1	1.31	1	0.22	1
0.45	0.122	2.55	1.95	2.53	1.93	0.44	1.95
0.65	0.273	5.32	4.06	5.23	3.99	0.91	4.06
0.95	0.536	15.6	11.9	15.1	11.6	2.69	11.9

Inside (tunneling) crossover, $S=30.25$, $p=2$.

$kT/\hbar\omega_0$	$\langle m\rangle$	$10^9 W_{p,z}$		$10^9 W_{p,\partial/\partial z}$		$10^9 L_p$	
0	0	0.440	1	0.440	1	0.0011	1
0.25	0.0187	7.74	17.6	5.34	12.1	0.078	71.2
0.35	0.0609	180.0	410.0	84.0	192.0	3.4	3080.0

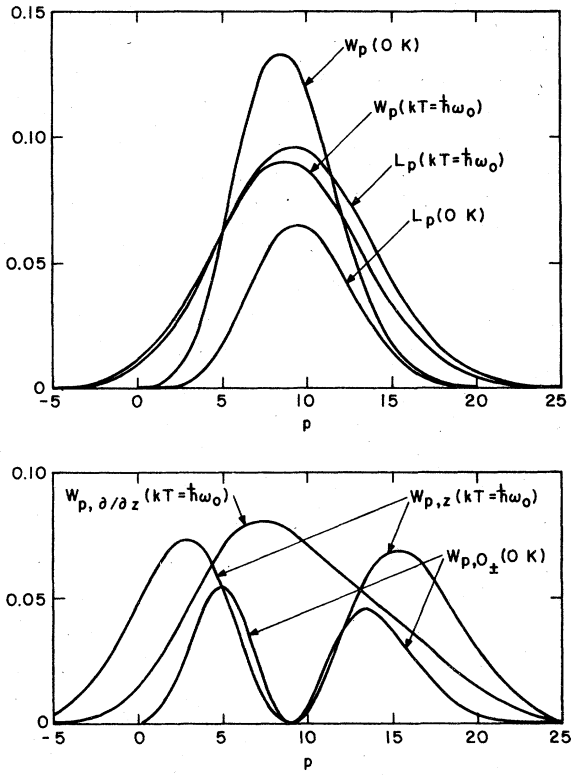

FIG. 1. Distributions W_p, L_p, $W_{p,z}$, and $W_{p,\partial/\partial z}$ for the large offset $S=9$. These distributions give the transition-rate nuclear factors for the operators 1, z, and $\partial/\partial z$ in single and multiple coordinates. See Eqs. (6) and the associated text.

has this node filled in by its

$$-2S\langle 1+m\rangle\langle m\rangle(W_{p-1}-2W_p+W_{p+1})$$

term in Eq. (3) and reverts to a single broad band similar to W_p and L_p.

Thus, the effect of combining L_p with $W_{p,O_\pm}$ in forming $M_{p,O_\pm}$ is to fill in any node at $p=S$. Therefore, compared to one-coordinate $W_{p,O_\pm}$, the multiple-coordinate distributions $M_{p,O_\pm}$ look more like the operator-1 distribution W_p.

The distributions W_p, $W_{p,O_\pm}$, and L_p are shown in Table II for cases of small offset ($S=0.2$, 0.04, and $\to 0$). The $S\to 0$ behaviors, derived in Sec. III, are $W_p=\delta_{p,0}$ and

$$W_{p,O_\pm}=L_p=\tfrac{1}{2}(\langle 1+m\rangle\delta_{p,+1}+\langle m\rangle\delta_{p,-1})\ .$$

The values 0.2 and 0.04 for S are small in the sense that, for the Condon-approximation operator 1, the zero-phonon line W_0 is strong, and the phonon side bands $W_{p\neq 0}$ are weak. However, for the operators $O_\pm$, the distributions $W_{p,O_\pm}$ differ from their $S\to 0$ limiting distribution. The limiting distributions were calculated assuming that the wave function overlap integrals $\langle u_n|v_m\rangle$ approximated δ_{nm}. For given S, the exact $\langle u_n|v_m\rangle$ matrix can be computed via the Manneback recursion formulas.[12,17] This $\langle u_n|v_m\rangle$ matrix for $S=0.2$ is shown in Table III. The elements are seen to differ greatly from δ_{nm}.

Returning to Table II, the largest departures from the limiting distributions occur for $W_{p,\partial/\partial z}$ at high temperature and are associated with the

$$-2S\langle 1+m\rangle\langle m\rangle(W_{p-1}-2W_p+W_{p+1})$$

term of $W_{p,\partial/\partial z}$ in Eq. (3). Because of the strong zero-phonon value W_0, this term is large for $p=0,\pm 1$, adding to the $W_{p,z}$ term of $W_{p,\partial/\partial z}$ in Eq. (3) for $p=0$ and subtracting for $p=\pm 1$. Thus, compared to its limiting distribution, $W_{p,\partial/\partial z}$ is larger for $p=0$ and smaller for $p=\pm 1$. These compensating behaviors maintain the sum $\sum_p W_{p,\partial/\partial z}$ independent of S. At $kT/\hbar\omega_0=1$, $W_{0,\partial/\partial z}$ is the largest $W_{p,\partial/\partial z}$ value for $S=0.2$ and, even for $S=0.04$, has the appreciable value of 0.15.

The next largest departures occur for $W_{p,O_\pm}$ for $p=1$ and 2. The term $[(p-S)^2/2S]W_p$ common to $W_{p,O_\pm}$ in Eq. (3) causes the ratio $W_{2,O_\pm}/W_{1,O_\pm}$ to be larger than W_2/W_1. This effect increases with S and is not very sensitive to the temperature. For example, for $S=0.2$, $W_{2,O_\pm}/W_{1,O_\pm}$ is greater than 0.5 at every temperature.

The L_p distribution deviates less from the limiting distribution than $W_{p,O_\pm}$ do. Thus, the multiple-coordinate weights $M_{p,O_\pm}$ in Eq. (6) deviate less from the limiting distribution than $W_{p,O_\pm}$ do. That is, departures from the limiting distribution are smaller in multiple coordinates.

V. ESTABLISHING $W_{p,O_\pm}$ vs $M_{p,O_\pm}$ EXPERIMENTALLY

The largest differences between single- and multiple-coordinate nuclear factors $W_{p,O_\pm}$, $M_{p,O_\pm}$ occur for S large.

For the z operator for S large, $W_{p,z}$ vs p has a node at $p=S$ with maxima on both sides, and $M_{p,z}$ has this node filled in by γL_p at every temperature. These z-operator distributions are expected for broad-band absorption spectra when the initial-state equilibrium configuration $z=0$ is a high-symmetry point and when the electronic integral for the transition is zero at $z=0$ and proportional to displacements z off this point. We are not aware of an absorption spectrum that shows the double-maximum $W_{p,z}$ behavior. Thus, experimental data appear to exclude a one-coordinate description $W_{p,z}$ or a multiple-coordinate description $M_{p,z}$ with γ small. A multiple-coordinate

TABLE II. W_p, $W_{p,z}$, $W_{p,\partial/\partial z}$, and L_p distributions for the small offsets $S=0.2$, 0.04, and $S\to 0$.

p	0 K			$kT/\hbar\omega_0=1$			
	W_p	$W_{p,O\pm}$	L_p	W_p	$W_{p,z}$	$W_{p,\partial/\partial z}$	L_p
$S=0.2$							
−3				0.000	0.004	0.003	0.001
−2				0.004	0.054	0.029	0.022
−1	0	0	0	0.077	0.277	0.084	0.199
0	0.819	0.082	0.000	0.673	0.067	0.458	0.122
1	0.164	0.262	0.409	0.209	0.334	0.229	0.542
2	0.016	0.133	0.082	0.033	0.266	0.212	0.166
3	0.001	0.021	0.008	0.004	0.068	0.058	0.026
4		0.002	0.000	0.000	0.010	0.009	0.003
5					0.001	0.001	0.000
$S=0.04$							
−2				0.000	0.013	0.011	0.006
−1	0	0	0	0.021	0.289	0.224	0.268
0	0.961	0.019	0.000	0.918	0.018	0.148	0.034
1	0.038	0.443	0.480	0.058	0.669	0.610	0.727
2	0.001	0.037	0.019	0.002	0.088	0.084	0.046
3		0.001	0.000	0.000	0.004	0.004	0.002
$S\to 0$							
−2	0		0	0		0	
−1	0		0	0		0.291	
0	1		0	1		0	
1	0		0.5	0		0.791	
2	0		0	0		0	

TABLE III. The matrix of wave function overlap integrals $\langle u_n|v_m\rangle$ for $S=0.2$. The omitted elements for $n<m$ are given by $\langle u_\alpha|v_\beta\rangle=(-1)^{\alpha+\beta}\langle u_\beta|v_\alpha\rangle$.

	$m=0$	1	2	3	4	5
$n=0$	0.905					
1	0.405	0.724				
2	0.128	0.515	0.561			
3	0.033	0.207	0.565	0.415		
4	0.007	0.063	0.273	0.582	0.285	
5	0.002	0.016	0.094	0.328	0.578	0.169
6	0.000	0.004	0.026	0.126	0.373	0.558
7		0.001	0.006	0.039	0.159	0.410
8			0.001	0.010	0.052	0.190
9				0.002	0.014	0.067
10				0.000	0.004	0.020

description $M_{p,z}$ with γ near 1 would describe these spectra. However, so would models with many different phonon energies $\hbar\omega$. We have been exploring such multiple-$\hbar\omega$ models numerically (not reported here) and find that for them the z-operator node is readily filled in.

For the $\partial/\partial z$ operator for S large, $W_{p,\partial/\partial z}$ vs p has a double maximum like $W_{p,z}$ at low temperatures, but the center cusp near $p=S$ is filled in with increasing temperature. For $M_{p,\partial/\partial z}$, the cusp is filled in by γL_p at every temperature. The $\partial/\partial z$ operator is expected for nonradiative transitions. These transitions will be much harder to study than z-operator absorption spectra. To obtain the p spectrum of nonradiative transitions, multiple transitions with different energy gaps $p\,\hbar\omega_0$ are needed. These multiple transitions can be obtained either from the same activator transition in several related hosts or from a single luminescence center with several related nonradiative transitions such as Eu^{3+} charge-transfer state (CTS) $\rightarrow {}^5D_j$ feeding. In either case, multiple electronic factors will be present, and it will be difficult to distinguish the p spectrum of the nuclear factor from different values of the electronic factors. However, since the temperature dependences of the rates arise from the nuclear factors, electronic factors determined empirically at one temperature might be used at another.

For p near S, nonradiative transitions are fast bottom crossovers with rates $10^{10}-10^{13}$ sec^{-1}. Thus, measuring the same transition singly in several related hosts will require rise-time equipment with picosecond capability. On the other hand, if one measures several competing transitions in a single center such as Eu^{3+} CTS $\rightarrow {}^5D_j$ feeding, one deals only with the relative rates into the several ${}^5D_j$ states. These relative rates can be inferred from the proportions of the ${}^5D_j$ emissions.

Our own experience has been with the Eu^{3+} CTS $\rightarrow {}^5D_j$ [21] and the analogous Sm^{2+} $5d\rightarrow {}^5D_1, {}^5D_0$ feeding fractions,[22] not with z-operator-dominated absorption spectra. We have no new feeding-fraction data taken specifically to distinguish among W_p, $W_{p,\partial/\partial z}$, and $M_{p,\partial/\partial z}$. The existing data give no evidence that crossovers close to the CTS or $5d$ minimum (p close to S) are avoided. For $BaCl_2$:Sm^{2+}, the simple W_p distribution described the observed ${}^5D_1, {}^5D_0$ feeding fractions better than $W_{p,\partial/\partial z}$ or $M_{p,\partial/\partial z}$.[23] For Y_2O_2S:Eu^{3+} and La_2O_2S:Eu^{3+}, the data were fit with unequal force constants and the operator 1, and we did not feel compelled to use the $\partial/\partial z$ operator.[21] Nevertheless, we expect that unequal force constants and the $\partial/\partial z$ operator will also give an adequate description.

The dip in the one-coordinate distributions $W_{p,O\pm}$ near $p=S$ does not require the force constants to be equal. We have computed one-coordinate, large-offset, unequal-force-constants examples numerically by the U,V-matrix method.[16,20] The distributions for the z and $\partial/\partial z$ operators still have the same dip, and this dip is again filled in at high temperatures for the $\partial/\partial z$ operator.

In summary, we expect that z- and $\partial/\partial z$-operator nodes at $p=S$ will not be confirmed experimentally and that interpretation of z- and $\partial/\partial z$-operator cases in single-$\hbar\omega_0$ models will require the multiple-coordinate functions $M_{p,O\pm}$ with γ near 1. Furthermore, we expect that interpretations through multiple-coordinate, multiple-$\hbar\omega$ models will not be very different from $M_{p,O\pm}$ with γ near 1 and that, in so far as these differences can be resolved experimentally, multiple-$\hbar\omega$ interpretations will be preferred.

VI. VIEW OF EQ. (4)

This paper concerns rate formulas derived exactly from rate (4). However, Eq. (4) itself is not exact, and we comment here on our attitude toward Eq. (4).

Rate (4) could be construed as the golden rule rate resulting from quantum-mechanical perturbation theory[24] plus approximation of the initial- and final-state wave functions ψ_i, ψ_f as the products $\psi_i=\phi_i v_1 v_2 \cdots v_N$, $\psi_f=\phi_f u_1 u_2 \cdots u_N$, where ϕ_i, ϕ_f are the initial and final electronic wave functions, $v_1, v_2, \cdots, v_N$ and $u_1, u_2, \cdots, u_N$ are the offset initial and final wave functions of N independent harmonic oscillators (nuclear coordinates) with the same phonon energy $\hbar\omega_0$, and the operator O is the resultant of the integration over the electronic coordinates. Indeed, Condon used rate (4) with $N=1$ and $O=$ constant for his quantum-mechanical treatment[25] of transition rates in diatomic molecules.

However, we view Eq. (4) as a simple model of transition rates even if it cannot be well argued from perturbation theory. For one thing, a continuous spectrum of phonon energies is needed to obtain conservation of energy in the transition. We believe that such a continuous spectrum is always present, yet it does not appear explicitly in Eq. (4). There may be instances where the transition energy mismatch is bridged mainly by p phonons of equal or nearly equal energy $\hbar\omega_0$ so that Eq. (4) might then be justified from perturbation theory. However, if phonons with different energies participate in the transition, we would prefer a model containing these different energies and are interested in such models. Nevertheless, we still regard Eq. (4) with $\hbar\omega_0$ some average or effective phonon energy as an appropriate first model whose predictions can be calculated accurately and compared with experiment.

The situation is analogous to that occurring in the theory of specific heats.[26] For specific heats, the Einstein lattice corresponds to the single-$\hbar\omega_0$ model here

with $N \rightarrow$ large. This Einstein lattice gives the specific heat proportional to the temperature derivative of $\langle m \rangle$ in Eq. (5) and, accordingly, going to zero at low temperature. However, to obtain the accurate low-temperature T^3 behavior of measured specific heats, a Debye lattice with phonon density of states proportional to $(\hbar\omega)^2$ is required. Although one therefore prefers the Debye lattice, the Einstein lattice is an appropriate first model and certainly deserves attention before going on to the Debye model.

Rate (4) contains the basic parameters of transition rates (energy mismatch $p\,\hbar\omega_0$, Franck-Condon offset S, and temperature T). Moreover, rates derived from Eq. (4) depend strongly on these parameters. We think the preferred present course is to learn these strong dependences from Eq. (4) and, by comparing these predictions with experiment, to see how far the simple model (4) goes toward accounting for observed transition rates.

With respect to specific operators O, we suppose, like Condon,[25] that the operator can be expressed in a power series about the equilibrium position of the initial vibrational state

$$O = a_0 + a_1 z + a_2 z^2 + \cdots \quad . \tag{26}$$

The Condon-approximation operator O = constant is the first term of this series. If the symmetry of the initial state is such that $a_0 = 0$, then the linear operator z is the first term of the remaining series.

We investigate the $\partial/\partial z$ operator for nonradiative transitions because, as the operator driving these transitions, a neglected term in the adiabatic approximation proportional to $\partial/\partial z$ is commonly recommended.[1,18,27]

We treat the z and $\partial/\partial z$ operators together because they are similar mathematically as opposed to physically. We have no reason to suggest z for nonradiative transitions. Nevertheless, we believe one should be open-minded about the nonradiative operator. In spite of the theoretical bias for $\partial/\partial z$, O = constant seems to fit experimental data better.

VII. CONCLUSIONS

For single-$\hbar\omega_0$ models of transition rates, the known one-coordinate nuclear factors are used to derive the corresponding nuclear factors for any number of coordinates N. For the operator 1, the nuclear factor is the HRP W_p function for any N. For the operators $O_+ = z$, $O_- = \partial/\partial z$, the nuclear factors $W_{p,O_\pm}$ for one coordinate and $M_{p,O_\pm}$ for $N \geq 2$ are related by

$$M_{p,O_\pm} = (1-\gamma)\, W_{p,O_\pm} + \gamma L_p \quad .$$

$W_{p,O_\pm}$ and L_p are the W_p-function combinations in Eqs. (3). The parameter γ lies between 0 and 1. The $\partial/\partial z$-operator factor $M_{p,\partial/\partial z}$ agrees with factors derived for 10^{22} coordinates by Huang and Rhys and by Perlin.

The largest differences between $W_{p,O_\pm}$ and $M_{p,O_\pm}$ are in the region p near S for S large. $W_{p,z}$ has a double maximum with a node at $p=S$. $M_{p,z}$ has this node filled in by γL_p, where for S large L_p is similar to W_p and has a single maximum near $p=S$. $W_{p,\partial/\partial z}$ is similar to $W_{p,z}$ at low temperatures with a node at $p=S$. This node is filled in at high temperatures. $M_{p,\partial/\partial z}$ has this node filled in by γL_p at every temperature.

In the limit $S \rightarrow 0$, we have

$$W_{p,O_\pm} = L_p = M_{p,O_\pm} = \tfrac{1}{2}(\langle 1+m \rangle \delta_{p,+1} + \langle m \rangle \delta_{p,-1}) \quad ,$$

that is, lines are only at $p = \pm 1$. For S values near 0.1 typical of $4f \rightarrow 4f$ and $3d \rightarrow 3d$ narrow-line transitions, transition weight is spread to nearby p values, especially to $p=0$ for $W_{p,\partial/\partial z}$ at high temperatures and to $p=2$ for $W_{p,O_\pm}$ at every temperature.

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APPENDIX A. $X_{p,O_\pm}$ FORMULA

The single-coordinate quantity $X_{p,O_\pm}$ is defined in Eq. (10). Using the $O_\pm$ matrix elements (8), Eq. (10) becomes

$$X_{p,O_\pm} = \sum_{m=m_0}^{+\infty} (\tfrac{1}{2}m)^{1/2} \langle u_{p+m} | v_m \rangle \langle u_{p+m} | v_{m-1} \rangle (1-r) r^m$$

$$\pm \sum_{m=m_0}^{+\infty} [\tfrac{1}{2}(m+1)]^{1/2} \langle u_{p+m} | v_m \rangle \langle u_{p+m} | v_{m+1} \rangle (1-r) r^m = r Y_{p+1} \pm Y_p = \frac{\langle m \rangle}{\langle 1+m \rangle} Y_{p+1} \pm Y_p \quad , \tag{A1}$$

where

$$Y_p \equiv \sum_{m=m_0}^{\infty} [\tfrac{1}{2}(m+1)]^{1/2} \langle u_{p+m}|v_m\rangle \times \langle u_{p+m}|v_{m+1}\rangle (1-r)\, r^m . \quad \text{(A2)}$$

Y_p can be evaluated from one of the Manneback recursion formulas[12,17] for the overlap integrals $\langle u_n|v_m\rangle$, namely, the first of Eqs. (9) of Ref. 12. This equation is, for n written as $p+m$,

$$(p+m)^{1/2}\langle u_{p-1+m}|v_m\rangle = (m+1)^{1/2}\langle u_{p+m}|v_{m+1}\rangle + S^{1/2}\langle u_{p+m}|v_m\rangle . \quad \text{(A3)}$$

If Eq. (A3) is squared and then operated on with $\sum_{m=m_0}^{+\infty}(1-r)\, r^m$, where m_0 is the larger of 0 and $-p$, one obtains

$$(p+\langle m\rangle_{p-1})\, W_{p-1} = r^{-1}\langle m\rangle_{p-1} W_{p-1} + SW_p + 2^{3/2}S^{1/2}Y_p , \quad \text{(A4)}$$

where W_p is defined by Eq. (4) with $N=1$, $O=1$, Y_p by Eq. (A2), and $\langle m\rangle_p$ by

$$\langle m\rangle_p \equiv W_p^{-1}\sum_{m=m_0}^{\infty} m\,\langle u_{p+m}|v_m\rangle^2 (1-r)\, r^m . \quad \text{(A5)}$$

The average $\langle m\rangle_p$ is evaluated in Eqs. (21) and (26) of Ref. 20 and is

$$\langle m\rangle_p = \langle m\rangle + S\langle 1+m\rangle\langle m\rangle\, W_p^{-1}(W_{p-1} - 2W_p + W_{p+1}) . \quad \text{(A6)}$$

Using from Eq. (5) $r^{-1}-1 = \langle m\rangle^{-1}$ and then both Eq. (A6) and the HRP W_p recursion formula (1) rewritten with $p \to p-1$, Eq. (A4) becomes

$$2^{3/2}S^{1/2}Y_p = (p - \langle m\rangle^{-1}\langle m\rangle_{p-1})\, W_{p-1} - SW_p = (p-1)\, W_{p-1} - S\langle 1+m\rangle(W_{p-2} - 2W_{p-1} + W_p) - SW_p = 2S\langle 1+m\rangle(W_{p-1} - W_p) . \quad \text{(A7)}$$

Inserting Eq. (A7) in Eq. (A1), one obtains the desired $X_{p,O_\pm}$ formula in Eq. (10).

APPENDIX B. EXPRESSION OF $W_{p,O_\pm}$ AS LINEAR COMBINATIONS OF W_p FUNCTIONS WITH COEFFICIENTS INDEPENDENT OF p

The simple formulas for $W_{p,O_\pm}$ in Eq. (3) contain p as an explicit coefficient of W_p in the term $[(p-S)^2/2S]W_p$. This p-containing coefficient can be avoided by expanding this term via the HRP W_p recursion formula (1). The expansion is

$$\begin{aligned} W_{p,z} &= \frac{1}{2S}(p-S)^2 W_p = \tfrac{1}{2}(p-S)\left[\frac{p}{S}W_p - W_p\right] = \tfrac{1}{2}(p-S)(\langle 1+m\rangle W_{p-1} - W_p - \langle m\rangle W_{p+1}) \\ &= \tfrac{1}{2}[\langle 1+m\rangle (p-1+1-S) W_{p-1} - (p-S)W_p - \langle m\rangle (p+1-1-S) W_{p+1}] \\ &= \tfrac{1}{2}(\langle 1+m\rangle W_{p-1} + \langle m\rangle W_{p+1}) + \tfrac{1}{2}S[\langle 1+m\rangle(\langle 1+m\rangle W_{p-2} - W_{p-1} - \langle m\rangle W_p) \\ &\quad - (\langle 1+m\rangle W_{p-1} - W_p - \langle m\rangle W_{p+1}) - \langle m\rangle(\langle 1+m\rangle W_p - W_{p+1} - \langle m\rangle W_{p+2})] \\ &= L_p + S\sum_{i=-2}^{+2}\alpha_{i,z} W_{p+i} , \end{aligned} \quad \text{(B1)}$$

where L_p is the W_p-function combination in Eq. (3), and the $\alpha_{i,z}$ are coefficients depending only on $\langle m\rangle$. Since $W_{p,z}$ and $W_{p,\partial/\partial z}$ are related as in Eq. (3), $W_{p,\partial/\partial z}$ can also be written in the form

$$W_{p,\partial/\partial z} = L_p + S\sum_{i=-2}^{+2}\alpha_{i,\partial/\partial z} W_{p+i} , \quad \text{(B2)}$$

where the $\alpha_{i,\partial/\partial z}$ are coefficients depending only on $\langle m\rangle$. The explicit expressions for the temperature coefficients $\alpha_{i,O_\pm}$ are, from Eqs. (B1) and (3),

$$\begin{aligned} &\alpha_{-2,z} = \tfrac{1}{2}\langle 1+m\rangle^2, \quad \alpha_{-2,\partial/\partial z} = \tfrac{1}{2}\langle 1+m\rangle^2 , \\ &\alpha_{-1,z} = -\langle 1+m\rangle , \quad \alpha_{-1,\partial/\partial z} = -\langle 1+m\rangle\langle 1+2m\rangle , \\ &\alpha_{0,z} = \tfrac{1}{2} - \langle 1+m\rangle\langle m\rangle , \quad \alpha_{0,\partial/\partial z} = \tfrac{1}{2} + 3\langle 1+m\rangle\langle m\rangle , \\ &\alpha_{+1,z} = \langle m\rangle , \quad \alpha_{+1,\partial/\partial z} = -\langle m\rangle\langle 1+2m\rangle , \\ &\alpha_{+2,z} = \tfrac{1}{2}\langle m\rangle^2, \quad \alpha_{+2,\partial/\partial z} = \tfrac{1}{2}\langle m\rangle^2 . \end{aligned} \quad \text{(B3)}$$

APPENDIX C. EVALUATION OF $\sum_{p_1=-\infty}^{+\infty} X_{p_1,O_1\pm} X_{p_2,O_2\pm}$ FOR $p_1+p_2=p$

$X_{p,O\pm}$ is given in Eq. (10) which can be written in the form

$$X_{p,O\pm} = (\tfrac{1}{2}S)^{1/2} \sum_{i=-1}^{+1} \beta_{i,O\pm} W_{p+i} , \tag{C1}$$

where

$$\beta_{-1,O\pm} = \pm \langle 1+m \rangle , \quad \beta_{0,O\pm} = \langle m \rangle \mp \langle 1+m \rangle ,$$

and

$$\beta_{+1,O\pm} = - \langle m \rangle .$$

Hence, making use of the HRP W_p-function reproductive formula (12),

$$\begin{aligned} \sum_{p_1} X_{p_1,O_1\pm} X_{p_2,O_2\pm} &= (S_1S_2)^{1/2} \tfrac{1}{2} \sum_{p_1} \left[\sum_{i=-1}^{+1} \beta_{i,O\pm} W_{p_1+i}(S_1, \langle m \rangle) \right] \left[\sum_{j=-1}^{+1} \beta_{j,O\pm} W_{p_2+j}(S_2, \langle m \rangle) \right] \\ &= (S_1S_2)^{1/2} \sum_{i=-1}^{+1} \sum_{j=-1}^{+1} \tfrac{1}{2} \beta_{i,O\pm} \beta_{j,O\pm} W_{p+i+j}(S_1+S_2, \langle m \rangle) \\ &= (S_1S_2)^{1/2} \sum_{i=-2}^{+2} \alpha_{i,O\pm} W_{p+i}(S_1+S_2, \langle m \rangle) , \end{aligned} \tag{C2}$$

where the $\alpha_{i,O\pm}$ are readily verified to be the $\alpha_{i,O\pm}$ given explicitly in Eq. (B3).

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