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Derivation of closed analytical expressions for Rosen–Morse Franck–Condon factors

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The expressions for Rosen–Morse Franck–Condon factors derived previously yield a double sum with alternating terms. For higher values of the quantum number the numerical calculation of the Franck–Condon factors by electronic computers using these expressions leads to numerical overflow inspite of the use of double-precision (32 digits) arithmetic. High values for the quantum number in the final ground state of the Rosen–Morse potential occur in molecular nonradiative rate calculations. Furthermore, the expressions show a lack of clearness with respect to the parameters of the potential. For out-of-plane modes exact closed form expressions and exact recurrence relations are derived. Asymptotic expressions for the matrix elements are calculated. Exact closed form expressions for matrix elements with quantum numbers which correspond to regions close to the dissociation barrier are given.

1. Introduction

Recent calculations of dissociation yields of H atoms in benzene [23] as well as of internal conversion rates [24] in benzene have shown the dominating influence of out-of-plane modes. Studies of Moore et al. [9] found the out-of-plane modes to be similarly important in HFCO. When large percentages of the excitation energy are accumulated in a single out-of-plane mode with low frequency, matrix elements with high quantum numbers become increasingly important. In such cases, the final quantum numbers can assume values of 80 and higher as is indeed the case, for example, in benzene. A double-precision arithmetic (32 digits) fails, however, already in calculating matrix elements with quantum numbers of about 35–40. It has been the aim of this work to derive an analytic solution for the evaluation of the necessary matrix elements, including those which correspond to energy regions near the dissociation barrier. As a suitable potential for the out-of-plane vibrations a Rosen–Morse potential can be used. In recent years, wave functions, kernels, path-integral expressions and coherent state analysis have been presented for this potential by different authors [2–15,17–21,25,26,28–33,35,37,38]. However, very few studies of numerical procedures for the calculation of Rosen–Morse Franck–Condon factors have been performed. Only very recently Zuniga et al. [39] have presented recurrence formulas for Rosen–Morse Franck–Condon factors and they have pointed out the numerical difficulties in computing the double summation, gamma functions and factorials. The solutions which are presented below offer not only exact analytical expressions but allow also to avoid the double summations. Especially the summation with repect to very high final quantum numbers is presented in closed form. The resulting short analytic expressions can be easily examined with respect to the dependency on the parameters of the potential. In a subsequent paper Rosen–Morse oscillators with diffferent operators including powers of the hyperbolic functions as well as derivative operators will be studied [22]. Closed form solutions for the case of different anharmonicities in the two wave functions of the integrand have been developed as well.

2. Theoretical considerations

The calculation of $S_1 \rightsquigarrow S_0$ nonradiative rates involving anharmonic out-of-plane vibrations require a suitable form of the potential energy. The Rosen–Morse potential [36] shown in figure 1 has been applied to describe the out-of-plane vibrations in molecules:

$$V(x) = -V_0 \frac{1}{\cosh^2(\alpha x)}. \tag{1}$$

This form is more appropriate than the harmonic oscillator potential, because for high excitations the molecule will dissociate along the corresponding coordinate.

The exact energy eigenvalues and normalized eigenfunctions of the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{V_0}{\cosh^2(\alpha x)}\right]\psi(x) = E'\psi(x), \tag{2}$$

have been given by Nieto [31]:

$$E_n^{'} = -\frac{\hbar^2\alpha^2}{2\mu}\left[-\left(n+\frac{1}{2}\right) + \frac{1}{2}\sqrt{1+\frac{8\mu V_0}{\alpha^2\hbar^2}}\right]^2, \tag{3}$$

where μ is the reduced mass, V_0 the dissociation energy, and α the anharmonicity constant. By introducing the relation

$$\kappa = \frac{\hbar^2\alpha^2}{2\mu}, \tag{4}$$

one finds from equations (3) and (4)

$$\omega = \kappa\sqrt{1+\frac{4V_0}{\kappa}}. \tag{5}$$

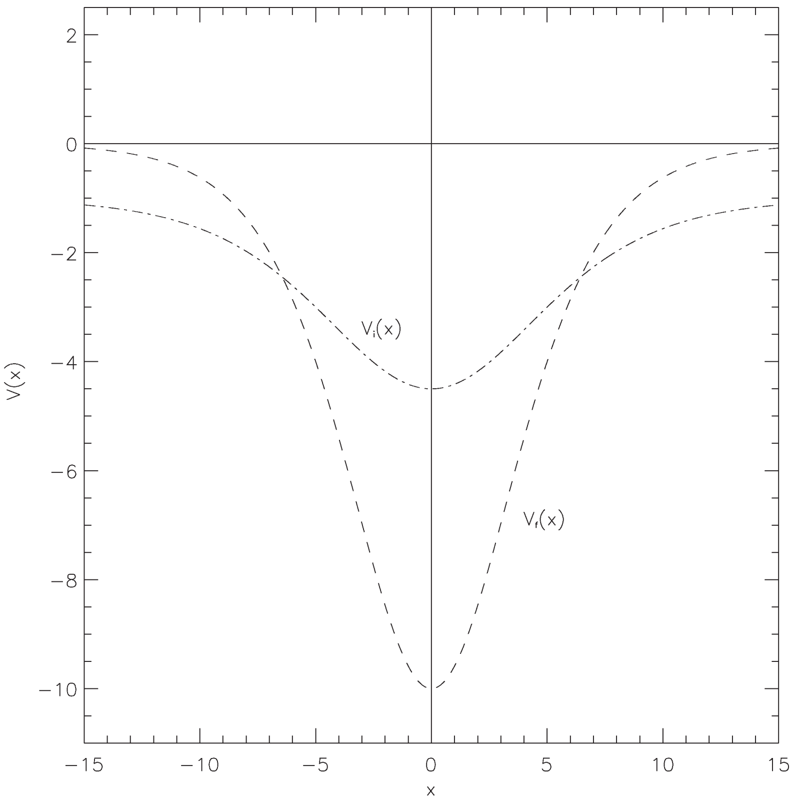

Figure 1. Schematic representation of the potential energy curves $V_\mathrm{i}(x)$ and $V_\mathrm{f}(x)$ for an out-of-plane mode (subscripts i, f denote the initial (excited) and final electronic states).

Equation (5) can be solved for κ,

$$\kappa \approx \frac{\omega^2}{4V_0}. \tag{6}$$

The energy E_n' can be expressed in the more conventional form:

$$E_n' = E_n - V_0 - \frac{\kappa}{4}, \quad E_n = \omega\left(n + \frac{1}{2}\right) - \kappa\left(n + \frac{1}{2}\right)^2. \tag{7}$$

The values for E_n and n have to obey the following restriction imposed by the dissociation limit V_0:

$$n_{\mathrm{max}} = \text{integral part of } \left(\frac{\omega}{2\kappa} - \frac{1}{2}\right). \tag{8}$$

Equation (2) leads to the following solution for the wave functions:

$$\psi(x) = \frac{N(n)}{\cosh^s(\alpha x)} f(\alpha x), \quad s = \frac{1}{2}\left(-1 + \frac{\omega}{\kappa}\right), \tag{9}$$

where $N(n)$ is the normalization constant and $f_{\mathrm{e},n}(\alpha x)$ and $f_{\mathrm{o},n}(\alpha x)$ are hypergeometric functions for even and odd n (see equations (15.5.3) and (15.5.4) of Abramowitz and Stegun (AS) [1]):

$$f_{\mathrm{e},n}(\alpha x) = {}_2F_1\left(-\frac{n}{2}, \frac{n}{2} - s; \frac{1}{2}; -\sinh^2(\alpha x)\right),\quad n = 0, 2, 4, \ldots, \tag{10}$$

$$f_{\mathrm{o},n}(\alpha x) = \sinh(\alpha x)\,{}_2F_1\left(-\frac{n-1}{2}, \frac{n-1}{2} - s + 1; \frac{3}{2}; -\sinh^2(\alpha x)\right),\quad n = 1, 3, 5, \ldots. \tag{11}$$

When the first label n in a hypergeometric function is a negative integer, then the hypergeometric function can be expressed as finite power series by using equations (15.4.1) and (15.5.3) of AS [1].

For even n one obtains the solutions

$$\psi_{\mathrm{e},n}(x) = \frac{N_{\mathrm{e}}(n)}{\cosh^s(\alpha x)} f_{\mathrm{e},n}(\alpha x), \tag{12}$$

$$f_{\mathrm{e},n}(\alpha x) = \left(\frac{n}{2}\right)!\,\Gamma\left(s - \frac{n}{2} + 1\right) \sum_{j=0}^{n/2} \frac{(-1)^j\, 2^{2j} \sinh^{2j}(\alpha x)}{(2j)!(n/2 - j)!\Gamma(s - n/2 - j + 1)}, \tag{13}$$

and for odd n one obtains

$$\psi_{\mathrm{o},n}(x) = \frac{N_{\mathrm{o}}(n)}{\cosh^s(\alpha x)} f_{\mathrm{o},n}(\alpha x), \tag{14}$$

$$f_{\mathrm{o},n}(\alpha x) = \left(\frac{n-1}{2}\right)!\,\Gamma\left(s - \frac{n-1}{2}\right) \sinh(\alpha x) \times \sum_{j=0}^{(n-1)/2} \frac{(-1)^j 2^{2j} \sinh^{2j}(\alpha x)}{(2j+1)!((n-1)/2 - j)!\Gamma(s - (n-1)/2 - j)}. \tag{15}$$

For the normalization constants $N_{\mathrm{e}}(n)$ and $N_{\mathrm{o}}(n)$ one finds the expressions

$$N_{\mathrm{e}}(n) = \left[\alpha \frac{(s-n)}{4^s} \frac{n!}{((n/2)!)^2} \frac{\Gamma(2s - n + 1)}{\Gamma^2(s - n/2 + 1)}\right]^{1/2}, \tag{16}$$

and

$$N_{\mathrm{o}}(n) = \left[\alpha \frac{(s-n)}{4^{s-1}} \frac{n!}{(((n-1)/2)!)^2} \frac{\Gamma(2s - n + 1)}{\Gamma^2(s - (n-1)/2)}\right]^{1/2}. \tag{17}$$

The transition matrix element for the nonradiative $S_1 \rightsquigarrow S_0$ process from the initial vibrational state $|n\rangle$ to the final state $\langle m|$ takes the form

$$\langle m|n\rangle = \int_{-\infty}^{\infty} \psi_{\mathrm{f},m}(x)\psi_{\mathrm{i},n}(x)\,\mathrm{d}x = \int_{-\infty}^{\infty} \frac{N(n,\alpha_\mathrm{i})N(m,\alpha_\mathrm{f})}{\cosh^{s_\mathrm{i}}(\alpha_\mathrm{i}x)\cosh^{s_\mathrm{f}}(\alpha_\mathrm{f}x)} f_{\mathrm{i},n}(\alpha_\mathrm{i}x) f_{\mathrm{f},m}(\alpha_\mathrm{f}x)\,\mathrm{d}x, \tag{18}$$

where the subscripts i and f refer to the initial (excited) and final (ground) states. As for harmonic potentials, the transitions from the excited vibronic state $|n\rangle$ to the final state $\langle m|$ are governed by selection rules. Non-zero matrix elements exist only for transitions between odd–odd and even–even states. For even wave functions, one thus obtains ($\beta = \alpha_\mathrm{i},\ \alpha = \alpha_\mathrm{f}$)

$$\begin{aligned}\langle m|n\rangle_\mathrm{e} = {} & \frac{\sqrt{\alpha\beta}}{2^{s_\mathrm{i}+s_\mathrm{f}-1}}\left[(s_\mathrm{i}-n)(s_\mathrm{f}-m)n!m!\Gamma(2s_\mathrm{i}-n+1)\Gamma(2s_\mathrm{f}-m+1)\right]^{1/2} \\ & \times \sum_{j=0}^{n/2}\sum_{i=0}^{m/2} \frac{(-1)^{i+j}4^{i+j}}{(n/2-j)!(2j)!\Gamma(s_\mathrm{i}-n/2-j+1)(m/2-i)!} \\ & \times \frac{1}{(2i)!\Gamma(s_\mathrm{f}-m/2-i+1)} \int_0^\infty \frac{\sinh^{2j}(\beta x)\sinh^{2i}(\alpha x)}{\cosh^{s_\mathrm{i}}(\beta x)\cosh^{s_\mathrm{f}}(\alpha x)}\,\mathrm{d}x,\end{aligned} \tag{19}$$

and for odd wave functions,

$$\begin{aligned}\langle m|n\rangle_\mathrm{o} = {} & \frac{\sqrt{\alpha\beta}}{2^{s_\mathrm{i}+s_\mathrm{f}-3}}\left[(s_\mathrm{i}-n)(s_\mathrm{f}-m)n!m!\Gamma(2s_\mathrm{i}-n+1)\Gamma(2s_\mathrm{f}-m+1)\right]^{1/2} \\ & \times \sum_{j=0}^{(n-1)/2}\sum_{i=0}^{(m-1)/2} \frac{(-1)^{i+j}\ 4^{i+j}}{((n-1)/2-j)!(2j+1)!} \\ & \times \frac{1}{\Gamma(s_\mathrm{i}-(n-1)/2-j)((m-1)/2-i)!(2i+1)!\Gamma(s_\mathrm{f}-(m-1)/2-i)} \\ & \times \int_0^\infty \frac{\sinh^{2j+1}(\beta x)\sinh^{2i+1}(\alpha x)}{\cosh^{s_\mathrm{i}}(\beta x)\cosh^{s_\mathrm{f}}(\alpha x)}\,\mathrm{d}x.\end{aligned} \tag{20}$$

For the general case $\alpha \neq \beta$, the solution of the integral in equations (19) and (20) cannot be expressed in closed form. As only very little is known about anharmonic force constants of out-of-plane modes [27,34], reasonable values for κ and, hence, for α are assumed in computational studies. The accuracy of these values is limited by uncertainties in the dissociation energies and in the experimental energies of higher members of the progression of the out-of-plane modes. However, by varying the values of α the influence of the anharmonicities of the out-of-plane modes on the matrix elements and nonradiative rates can be studied.

In a forthcoming paper the general case of $\alpha \neq \beta$ will be treated. The present study is restricted to the case $\alpha = \beta$. By inserting the analytical expressions for the integrals into equations (19) and (20), one obtains for even–even transitions

$$\begin{aligned}\langle m|n\rangle_{\mathrm{e}} = {} & \frac{\sqrt{\pi}}{2^{s_{\mathrm{i}}+s_{\mathrm{f}}}}\big[(s_{\mathrm{i}}-n)(s_{\mathrm{f}}-m)n!m!\Gamma(2s_{\mathrm{i}}-n+1) \\ & \times \Gamma(2s_{\mathrm{f}}-m+1)\big]^{1/2}\frac{1}{\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2)} \\ & \times \sum_{j=0}^{n/2}\sum_{i=0}^{m/2}\frac{(-1)^{i+j}\,\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-i-j)(2i+2j)!}{(n/2-j)!(2j)!\Gamma(s_{\mathrm{i}}-n/2-j+1)(m/2-i)!} \\ & \times \frac{1}{(2i)!\Gamma(s_{\mathrm{f}}-m/2-i+1)(i+j)!},\end{aligned} \tag{21}$$

and for odd–odd transitions

$$\begin{aligned}\langle m|n\rangle_{\mathrm{o}} = {} & \frac{\sqrt{\pi}}{2^{s_{\mathrm{i}}+s_{\mathrm{f}}-1}}\big[(s_{\mathrm{i}}-n)(s_{\mathrm{f}}-m)n!m!\Gamma(2s_{\mathrm{i}}-n+1) \\ & \times \Gamma(2s_{\mathrm{f}}-m+1)\big]^{1/2}\frac{1}{\Gamma((s_{\mathrm{i}}+s_{\mathrm{f}}+1)/2)} \\ & \times \sum_{j=0}^{(n-1)/2}\sum_{i=0}^{(m-1)/2}\frac{(-1)^{i+j}\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-j-i-1)(2j+2i+1)!}{((n-1)/2-j)!(2j+1)!\Gamma(s_{\mathrm{i}}-(n-1)/2-j)} \\ & \times \frac{1}{((m-1)/2-i)!(2i+1)!\Gamma(s_{\mathrm{f}}-(m-1)/2-i)(i+j)!}.\end{aligned} \tag{22}$$

In appendix B of [24] recurrence formulas and asymptotic expressions for equations (21) and (22) are presented.

The calculation of nonradiative transition rates in molecules show that even in case a 32 digit double-precision arithmetic is used numerical errors due to the numerical cancellation of alternating terms in the summation occur. These numerical errors occur especially when large basis sets are necessary in order to describe the out-of-plane modes. For benzene, for example, one has to evaluate matrix elements with final (ground state) quantum numbers as high as ≈75 for the ν_4 mode and ≈100 for the ν_{16} out-of-plane mode. In general, the quantum numbers of the excited state which enter the calculations of the matrix elements are rather low (e.g., <20 fo the ν_4 out-of-plane vibration in benzene which corresponds to an excess energy of about 7000 cm^{-1}).

In the following, a closed form expression for the summations over the high final quantum numbers m in equations (21) and (22) will be derived. One starts by replacing the hypergeometric functions in equations (10) and (11) by Jacoby polynomials as given by Gradshteyn and Ryzhik on [16, p. 1036, no. 8.962]:

$$\begin{aligned}&{}_2F_1\big(-n', -n'-\alpha; \beta+1; -\sinh^2(z)\big)\\&\quad= \frac{\Gamma(\beta+1)\Gamma(n'+1)}{\Gamma(n'+\beta+1)}\left(\frac{1}{\tanh^2(z)-1}\right)^{n'} P_{n'}^{\alpha,\beta}\big(2\tanh^2(z)-1\big).\end{aligned} \tag{23}$$

By inserting this expression into equation (18) and performing the transformation $y=\tanh^2(z)$ and $y=(1+t)/2$ one finds

$$\begin{aligned}\langle m|n\rangle_{\mathrm{e}} &= \pi N_{\mathrm{e}}(n)N_{\mathrm{e}}(m)(-1)^{(n+m)/2}\left(\frac{1}{2}\right)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-(n+m)/2-1/2}\\&\quad\times\frac{\Gamma(n/2+1)\Gamma(m/2+1)}{\Gamma(n/2+1/2)\Gamma(m/2+1/2)}\\&\quad\times\int_{-1}^{1}\mathrm{d}t\,(1-t)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-(n+m)/2-1}(1+t)^{-1/2}P_{n/2}^{s_{\mathrm{i}}-n,-1/2}(t)P_{m/2}^{s_{\mathrm{f}}-m,-1/2}(t),\end{aligned} \tag{24}$$

$$\begin{aligned}\langle m|n\rangle_{\mathrm{o}} &= \pi N_{\mathrm{o}}(n)N_{\mathrm{o}}(m)(-1)^{(m-1+n-1)/2}\left(\frac{1}{2}\right)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-(n-1+m-1)/2-1/2}\\&\quad\times\frac{\Gamma((n-1)/2+1)\Gamma((m-1)/2+1)}{\Gamma((n-1)/2+1+1/2)\Gamma((m-1)/2+1+1/2)}\\&\quad\times\int_{-1}^{1}(1-t)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-(n-1+m-1)/2-2}\sqrt{1+t}\,P_{(n-1)/2}^{s_{\mathrm{i}}-n,1/2}(t)P_{(m-1)/2}^{s_{\mathrm{f}}-m,1/2}(t).\end{aligned} \tag{25}$$

For the initial state Jacobi polynomials, the explicit summation form is inserted:

$$\begin{aligned}P_{n'}^{\alpha,\beta}(x) &= \frac{(-1)^{n'}}{2^{n'}}\,\Gamma(n'+\alpha+1)\,\Gamma(n'+\beta+1)\\&\quad\times\sum_{l=0}^{n'}\frac{(-1)^l(1-x)^{n'-l}(1+x)^l}{l!(n'-l)!\Gamma(n'+\alpha+1-l)\Gamma(\beta+1+l)}.\end{aligned} \tag{26}$$

By inserting (26) into equations (24) and (25) one finds

$$\begin{aligned}\langle m|n\rangle_{\mathrm{e}} &= \pi N_{\mathrm{e}}(m)N_{\mathrm{e}}(n)(-1)^{m/2}\left(\frac{1}{2}\right)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-m/2-1/2}\\&\quad\times\frac{\Gamma(n/2+1)\Gamma(m/2+1)\Gamma(s_{\mathrm{i}}-n/2+1)}{\Gamma(m/2+1/2)}\\&\quad\times\sum_{k=0}^{n/2}\frac{(-1)^k}{k!(n/2-k)!\Gamma(s_{\mathrm{i}}-n/2+1-k)\Gamma(1/2+k)}I_{\mathrm{e}}(t),\end{aligned} \tag{27}$$

$$
\begin{aligned}
\langle m|n\rangle_{\mathrm{o}} = {} & \pi N_{\mathrm{o}}(n)N_{\mathrm{o}}(m)(-1)^{(m-1)/2}\left(\frac{1}{2}\right)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-(m-1)/2+3/2} \\
& \times \frac{\Gamma((n-1)/2+1)\Gamma((m-1)/2+1)\Gamma(s_{\mathrm{i}}-(n-1)/2)}{\Gamma((m-1)/2+3/2)} \\
& \times \sum_{k=0}^{(n-1)/2} \frac{(-1)^k}{k!((n-1)/2-k)!\Gamma(s_{\mathrm{i}}-(n-1)/2-k)\Gamma(k+3/2)} I_{\mathrm{o}}(t), \quad (28)
\end{aligned}
$$

where

$$
\begin{aligned}
I_{\mathrm{e}}(t) &= \int_{-1}^{1} \mathrm{d}t\,(1-t)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-m/2-k-1}(1+t)^{k-1/2}P_{m/2}^{s_{\mathrm{f}}-m,-1/2}(t), \\
I_{\mathrm{o}}(t) &= \int_{-1}^{1} \mathrm{d}t\,(1-t)^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-(m-1)/2-k-2}(1+t)^{k+1/2}P_{(m-1)/2}^{s_{\mathrm{f}}-m,1/2}(t).
\end{aligned} \quad (29)
$$

The term $(1+t)^{k+1/2}$ in equations (29) is written as $(1+t)^{1/2}(1+t)^k$ and by developing

$$
(1+t)^k = (t-1+2)^k = \sum_{l=0}^{k} \binom{k}{l} 2^{k-l} (-1)^l (1-t)^l, \quad (30)
$$

one obtains from equations (29):

$$
\begin{aligned}
I_{\mathrm{e}}(t) &= \sum_{l=0}^{k} \binom{k}{l} 2^{k-l}(-1)^l \int_{-1}^{1} \mathrm{d}t\,(1-t)^{\rho_{\mathrm{e}}}(1+t)^{-1/2}P_{m/2}^{s_{\mathrm{f}}-m,-1/2}(t), \\
\rho_{\mathrm{e}} &= \frac{s_{\mathrm{f}}+s_{\mathrm{i}}}{2} - \frac{m}{2} - k + l - 1, \\
I_{\mathrm{o}}(t) &= \sum_{l=0}^{k} \binom{k}{l} 2^{k-l}(-1)^l \int_{-1}^{1} \mathrm{d}t\,(1-t)^{\rho_{\mathrm{o}}}(1+t)^{1/2}P_{(m-1)/2}^{s_{\mathrm{f}}-m,1/2}(t), \\
\rho_{\mathrm{o}} &= \frac{s_{\mathrm{f}}+s_{\mathrm{i}}}{2} - \frac{m-1}{2} - k + l - 2.
\end{aligned} \quad (31)
$$

Equations (31) have taken now a form which can be written as closed form expressions as shown by Gradshteyn in [16, p. 841, no. 4]:

$$
\begin{aligned}
I_{\mathrm{e}}(t) = {} & 2^{(s_{\mathrm{f}}+s_{\mathrm{i}})/2-1/2-m/2}\frac{\Gamma(m/2+1/2)k!}{(m/2)!} \\
& \times \sum_{l=0}^{k} \frac{(-1)^l\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-m/2-k+l)}{l!(k-l)!\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-k+1/2+l)} \\
& \times \frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+k-l)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2+1+k-l)}, \quad (32)
\end{aligned}
$$

$$
\begin{aligned}
I_{\rm o}(t) = {} & 2^{(s_{\rm f}+s_{\rm i})/2-(m-1)/2-1/2} \frac{\Gamma((m-1)/2+1+1/2)}{((m-1)/2)!} \\
& \times \sum_{l=0}^{k} \frac{(-1)^l \Gamma((s_{\rm f}+s_{\rm i})/2-(m-1)/2-1-k+l)}{l!(k-l)!\Gamma((s_{\rm f}+s_{\rm i})/2+1/2-k+l)} \\
& \times \frac{\Gamma((s_{\rm f}-s_{\rm i})/2+1+k-l)}{\Gamma((s_{\rm f}-s_{\rm i})/2-(m-1)/2+1+k-l)}.
\end{aligned}
$$

By inserting equations (32) into equations (27) and (28), respectively, one finally obtains for matrix elements with even quantum numbers:

$$
\begin{aligned}
\langle m|n\rangle_{\rm e} = {} & \pi(-1)^{m/2}\left(\frac{1}{2}\right)^{s_{\rm i}+s_{\rm f}} \\
& \times \left[\frac{(s_{\rm i}-n)(s_{\rm f}-m)\Gamma(2s_{\rm i}-n+1)\Gamma(2s_{\rm f}-m+1)n!m!}{\Gamma^2(s_{\rm f}-m/2+1)((m/2)!)^2}\right]^{1/2} \\
& \times \sum_{k=0}^{n/2} \frac{(-1)^k}{(n/2-k)!\Gamma(s_{\rm i}-n/2+1-k)\Gamma(k+1/2)} \\
& \times \sum_{l=0}^{k} \frac{(-1)^l \Gamma((s_{\rm f}+s_{\rm i})/2-m/2-k+l)}{(k-l)!l!\Gamma((s_{\rm f}+s_{\rm i})/2+1/2-k+l)} \\
& \times \frac{\Gamma((s_{\rm f}-s_{\rm i})/2+1+k-l)}{\Gamma((s_{\rm f}-s_{\rm i})/2-m/2+1+k-l)}.
\end{aligned}
\tag{33}
$$

In this derivation the summation over m with the many alternating terms is expressed in closed form. This can still be demonstrated more clearly in case $n = 0$:

$$
\begin{aligned}
\langle m|0\rangle_{\rm e} = {} & \sqrt{\pi}(-1)^{m/2}\left(\frac{1}{2}\right)^{s_{\rm i}+s_{\rm f}-1/2} \\
& \times \left[(s_{\rm f}-m)\frac{\Gamma(2s_{\rm i})}{\Gamma^2(s_{\rm i})}\frac{\Gamma(2s_{\rm f}-m+1)}{\Gamma^2(s_{\rm f}-m/2+1)}\frac{m!}{((m/2)!)^2}\right]^{1/2} \\
& \times \frac{\Gamma((s_{\rm f}+s_{\rm i})/2-m/2)}{\Gamma((s_{\rm f}+s_{\rm i})/2+1/2)}\Theta_{\rm e}(s_{\rm i},s_{\rm f}),
\end{aligned}
\tag{34}
$$

$$
\Theta_{\rm e}(s_{\rm i},s_{\rm f}) = \frac{\Gamma((s_{\rm f}-s_{\rm i})/2+1)}{\Gamma((s_{\rm f}-s_{\rm i})/2-m/2+1)}, \quad s_{\rm f} > s_{\rm i},
$$

$$
\Theta_{\rm e}(s_{\rm i},s_{\rm f}) = (-1)^{m/2}\frac{\Gamma((s_{\rm i}-s_{\rm f})/2+m/2)}{\Gamma((s_{\rm i}-s_{\rm f})/2)}, \quad s_{\rm f} < s_{\rm i}.
$$

The special case $s_{\rm f} = s_{\rm i}$ is given in appendix B. For the evaluation of the matrix elements with odd quantum numbers equivalent steps lead to

$$
\begin{aligned}
\langle m|n\rangle_{\mathrm{o}} = {} & \pi(-1)^{(m-1)/2}\left(\frac{1}{2}\right)^{s_{\mathrm{i}}+s_{\mathrm{f}}} \\
& \times \left[\frac{(s_{\mathrm{i}}-n)\Gamma(2s_{\mathrm{i}}-n+1)n!(s_{\mathrm{f}}-m)m!\Gamma(2s_{\mathrm{f}}-m+1)}{(((m-1)/2)!)^2\Gamma^2(s_{\mathrm{f}}-(m-1)/2)}\right]^{1/2} \\
& \times \sum_{k=0}^{(n-1)/2} \frac{(-1)^k}{((n-1)/2-k)!\Gamma(s_{\mathrm{i}}-(n-1)/2-k)\Gamma(k+3/2)} \\
& \times \sum_{l=0}^{k} \frac{(-1)^l\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-(m-1)/2-1-k+l)}{l!(k-l)!\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2-k+l)} \\
& \times \frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+k-l)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-(m-1)/2+1+k-l)},
\end{aligned} \tag{35}
$$

and the special case $n = 1$ takes the form

$$
\begin{aligned}
\langle m|1\rangle_{\mathrm{o}} = {} & \sqrt{\pi}(-1)^{(m-1)/2}\left(\frac{1}{2}\right)^{s_{\mathrm{i}}+s_{\mathrm{f}}-1} \\
& \times \left[\frac{(s_{\mathrm{i}}-1)\Gamma(2s_{\mathrm{i}})(s_{\mathrm{f}}-m)m!\Gamma(2s_{\mathrm{f}}-m+1)}{\Gamma^2(s_{\mathrm{i}})(((m-1)/2)!)^2\Gamma^2(s_{\mathrm{f}}-(m-1)/2)}\right]^{1/2} \\
& \times \frac{\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-(m-1)/2-1)}{\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2)}\Theta_{\mathrm{o}}(s_{\mathrm{i}},s_{\mathrm{f}}),
\end{aligned} \tag{36}
$$

$$
\begin{aligned}
\Theta_{\mathrm{o}}(s_{\mathrm{i}},s_{\mathrm{f}}) &= \frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-(m-1)/2+1)}, \quad s_{\mathrm{f}} > s_{\mathrm{i}}, \\
\Theta_{\mathrm{o}}(s_{\mathrm{i}},s_{\mathrm{f}}) &= (-1)^{(m-1)/2}\frac{\Gamma((s_{\mathrm{i}}-s_{\mathrm{f}})/2+(m-1)/2)}{\Gamma((s_{\mathrm{i}}-s_{\mathrm{f}})/2)}, \quad s_{\mathrm{f}} < s_{\mathrm{i}}.
\end{aligned}
$$

The special case $s_{\mathrm{f}} = s_{\mathrm{i}}$ is given in appendix B. An inspection of the double sum expression in equations (33) and (35) shows that it is possible to reduce the double sum expression to a simple single sum expression. By reordering the terms in the double summations one finds the following identities for even quantum numbers:

$$
\begin{aligned}
& \sum_{k=0}^{n/2} \frac{(-1)^k}{(n/2-k)!\Gamma(s_{\mathrm{i}}-n/2+1-k)\Gamma(k+1/2)} \\
& \quad \times \sum_{l=0}^{k} \frac{(-1)^k\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-m/2-k+l)}{(k-l)!l!\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2-k+l)} \\
& \quad \times \frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+k-l)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2+1+k-l)}
\end{aligned}
$$

$$= \frac{1}{\sqrt{\pi}} \sum_{l=0}^{n/2} \frac{(-1)^l \Gamma((s_\mathrm{f}+s_\mathrm{i})/2 - m/2 - l)\Gamma((s_\mathrm{f}-s_\mathrm{i})/2+1+l)}{\Gamma((s_\mathrm{f}+s_\mathrm{i})/2+1/2-l)\Gamma((s_\mathrm{f}-s_\mathrm{i})/2-m/2+1+l)} \times \sum_{k=l}^{n/2} \frac{2^{2k} k!}{(n/2-k)!\Gamma(s_\mathrm{i}-n/2+1-k)(2k)!(k-l)!}. \qquad (37)$$

Similarily, one obtains for the odd quantum numbers:

$$\sum_{k=0}^{(n-1)/2} \frac{(-1)^k}{((n-1)/2-k)!\Gamma(s_\mathrm{i}-(n-1)/2-k)\Gamma(k+3/2)} \times \sum_{l=0}^{k} \frac{(-1)^l \Gamma((s_\mathrm{f}+s_\mathrm{i})/2-(m-1)/2-1-k+l)}{(k-l)!l!\Gamma((s_\mathrm{f}+s_\mathrm{i})/2+1/2-k+l)} \times \frac{\Gamma((s_\mathrm{f}-s_\mathrm{i})/2+1+k-l)}{\Gamma((s_\mathrm{f}-s_\mathrm{i})/2-(m-1)/2+1+k-l)}$$
$$= \frac{1}{\sqrt{\pi}} \sum_{l=0}^{(n-1)/2} \frac{(-1)^l \Gamma((s_\mathrm{f}+s_\mathrm{i})/2-(m-1)/2-1-l)\Gamma((s_\mathrm{f}+s_\mathrm{i})/2+1+l)}{l!\Gamma((s_\mathrm{f}+s_\mathrm{i})/2+1/2-l)\Gamma((s_\mathrm{f}-s_\mathrm{i})/2-(m-1)/2+1+l)} \times \sum_{k=l}^{(m-1)/2} \frac{2^{2k+1} k!}{((n-1)/2-k)!(k-l)!\Gamma(s_\mathrm{i}-(n-1)/2-k)(2k+1)!}. \qquad (38)$$

Closed analytical expressions can be derived for the second summation in equations (37) and (38):

$$\sum_{k=l}^{n'} \frac{2^{2k}}{(n'-k)!(2k)!\Gamma(a-k+1)} \frac{k!}{(k-l)!} = \frac{n'!}{(2n')!} \frac{\Gamma(a)}{\Gamma(2a)} \frac{2^{2l}}{(n'-l)!} \frac{\Gamma(2a+2n'-2l)}{\Gamma(a-l+1)\Gamma(a+n'-l)}, \quad 0 \leqslant l \leqslant n', \qquad (39)$$

$$\sum_{k=l}^{n'} \frac{2^{2k}}{(n'-k)!\Gamma(b-k)(2k+1)!} \frac{k!}{(k-l)!} = \frac{n'!\Gamma(b)2^{2l}\Gamma(2b+2n'-2l)}{(2n'+1)!\Gamma(2b)(n'-l)!\Gamma(b-l)\Gamma(b+n'-l)}. \qquad (40)$$

Applying identities (39) and (40) to equations (37) and (38) one finds the final form for equations (33) and (35) which include only one summation in each formula. For the case of matrix elements with even quantum numbers one obtains

$$\langle m|n\rangle_{\mathrm{e}} = \sqrt{\pi}(-1)^{m/2}\left(\frac{1}{2}\right)^{s_{\mathrm{i}}+s_{\mathrm{f}}-1}\left[(s_{\mathrm{i}}-n)(s_{\mathrm{f}}-m)\frac{((n/2)!)^2}{n!}\frac{m!}{((m/2)!)^2}\right.$$
$$\left.\times\frac{\Gamma^2(s_{\mathrm{i}}-n/2+1)}{\Gamma(2s_{\mathrm{i}}-n+1)}\frac{\Gamma(2s_{\mathrm{f}}-m+1)}{\Gamma^2(s_{\mathrm{f}}-m/2+1)}\right]^{1/2}$$
$$\times\sum_{l=0}^{n/2}\frac{(-1)^l 2^{2l}\Gamma(2s_{\mathrm{i}}-2l)}{l!(n/2-l)!\Gamma(s_{\mathrm{i}}-n/2-l+1)\Gamma(s_{\mathrm{i}}-l)}$$
$$\times\frac{\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-m/2-l)}{\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2-l)}\frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+l)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2+1+l)},$$
$$s_{\mathrm{i}}\neq s_{\mathrm{f}},\ \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}-\frac{m}{2}+1+l\neq 0,-1,-2,\ldots, \tag{41}$$

and for the case with odd quantum numbers,

$$\langle m|n\rangle_{\mathrm{o}} = \sqrt{\pi}(-1)^{(m-1)/2}\left(\frac{1}{2}\right)^{s_{\mathrm{i}}+s_{\mathrm{f}}-1}\left[(s_{\mathrm{i}}-n)(s_{\mathrm{f}}-m)\frac{m!}{(((m-1)/2)!)^2}\right.$$
$$\left.\times\frac{(((n-1)/2)!)^2}{n!}\frac{\Gamma^2(s_{\mathrm{i}}-(n-1)/2)}{\Gamma(2s_{\mathrm{i}}-n+1)}\frac{\Gamma(2s_{\mathrm{f}}-m+1)}{\Gamma^2(s_{\mathrm{f}}-(m-1)/2)}\right]^{1/2}$$
$$\times\sum_{l=0}^{(n-1)/2}\frac{(-1)^l 2^{2l}\Gamma(2s_{\mathrm{i}}-2l)}{l!((n-1)/2-l)!\Gamma(s_{\mathrm{i}}-(n-1)/2-l)\Gamma(s_{\mathrm{i}}-l)}$$
$$\times\frac{\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-(m-1)/2-1-l)}{\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2-l)}\frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+l)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-(m-1)/2+1+l)},$$
$$s_{\mathrm{i}}\neq s_{\mathrm{f}},\ \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}-\frac{m-1}{2}+1+l\neq 0,-1,-2,\ldots. \tag{42}$$

Equations (41) and (42) are the exact solution for the Rosen–Morse matrix elements and Franck–Condon factors, respectively. The special cases $s_{\mathrm{f}}=s_{\mathrm{i}}$ and $(s_{\mathrm{f}}-s_{\mathrm{i}})/2=M$ (M integer) are given in appendix B.

Equations (41) and (42) can be expressed in a form which allows to apply recurrence relations for the numerical calculation. At the same time the matrix elements can be explicitely given in a composite form

$$\langle m|n\rangle_{\mathrm{e}} = \langle m|0\rangle_{\mathrm{e}}\phi_{\mathrm{e}}(n)\sum_{l=0}^{n/2}S_{\mathrm{e}}(l),\qquad \phi_{\mathrm{e}}(n)=\left[\frac{1}{n!}\frac{2(s_{\mathrm{i}}-n)\Gamma(2s_{\mathrm{i}})}{\Gamma(2s_{\mathrm{i}}-n+1)}\right]^{1/2}, \tag{43}$$

where

$$\begin{aligned} S_\mathrm{e}(0) &= 1, \\ S_\mathrm{e}(l+1) &= -\frac{1}{2}\frac{(n-2l)}{(l+1)}\frac{(2s_\mathrm{i}-n-2l)}{(2s_\mathrm{i}-2l-1)}\frac{(s_\mathrm{f}-s_\mathrm{i}+2l+2)}{(s_\mathrm{f}-s_\mathrm{i}-m+2l+2)} \\ &\quad\times \frac{(s_\mathrm{f}+s_\mathrm{i}-2l-1)}{(s_\mathrm{f}+s_\mathrm{i}-m-2l-2)} S_\mathrm{e}(l), \end{aligned} \tag{44}$$

$$\begin{aligned} \langle m|n\rangle_\mathrm{o} &= \langle m|1\rangle_\mathrm{o}\phi_\mathrm{o}(n)\sum_{l=0}^{(n-1)/2} S_\mathrm{o}(l), \\ \phi_\mathrm{o}(n) &= \left[\frac{1}{n!}\frac{(s_\mathrm{i}-n)}{(s_\mathrm{i}-1)}\frac{\Gamma(2s_\mathrm{i})}{\Gamma(2s_\mathrm{i}-n+1)}\right]^{1/2}, \end{aligned} \tag{45}$$

$$\begin{aligned} S_\mathrm{o}(0) &= 1, \\ S_\mathrm{o}(l+1) &= -\frac{1}{2}\frac{(n-2l-1)}{(l+1)}\frac{(2s_\mathrm{i}-n-1-2l)}{(2s_\mathrm{i}-1-2l)}\frac{(s_\mathrm{f}-s_\mathrm{i}+2+2l)}{(s_\mathrm{f}-s_\mathrm{i}-m+3+2l)} \\ &\quad\times \frac{(s_\mathrm{f}+s_\mathrm{i}-1-2l)}{(s_\mathrm{f}+s_\mathrm{i}-3-m-2l)} S_\mathrm{o}(l). \end{aligned} \tag{46}$$

The following recurrence relations for $\langle m|0\rangle_\mathrm{e}$ (equation (34)) and $\langle m|1\rangle_\mathrm{o}$ (equation (36)) hold:

$$\begin{aligned} \langle m+2|0\rangle_\mathrm{e} &= -\left[\frac{(m+1)}{(m+2)}\frac{(s_\mathrm{f}-m-2)}{(s_\mathrm{f}-m)}\frac{(2s_\mathrm{f}-m)}{(2s_\mathrm{f}-m-1)}\right]^{1/2} \\ &\quad\times \frac{(s_\mathrm{f}-s_\mathrm{i}-m)}{(s_\mathrm{f}+s_\mathrm{i}-m-2)}\langle m|0\rangle_\mathrm{e}, \\ \langle 0|0\rangle_\mathrm{e} &= \left[\frac{\Gamma(2s_\mathrm{i})}{\Gamma^2(s_\mathrm{i})}\frac{\Gamma(2s_\mathrm{f})}{\Gamma^2(s_\mathrm{f})}\right]^{1/2}\frac{\Gamma^2((s_\mathrm{f}+s_\mathrm{i})/2)}{\Gamma(s_\mathrm{i}+s_\mathrm{f})}. \end{aligned} \tag{47}$$

For $s_\mathrm{i}, s_\mathrm{f} \gg 1$, the matrix elements $\langle 0|0\rangle_\mathrm{e}$ can be approximated by

$$\langle 0|0\rangle_\mathrm{e} \approx \left[2\frac{\sqrt{s_\mathrm{i}s_\mathrm{f}}}{s_\mathrm{i}+s_\mathrm{f}}\right]^{1/2}. \tag{48}$$

Similarily, one can deduce the equivalent recurrence relations for the odd matrix element $\langle m|1\rangle_\mathrm{o}$:

$$\begin{aligned} \langle m+2|1\rangle_\mathrm{o} &= \left[\frac{(m+2)}{(m+1)}\frac{(s_\mathrm{f}-m-2)}{(s_\mathrm{f}-m)}\frac{(2s_\mathrm{f}-m-1)}{(2s_\mathrm{f}-m)}\right]^{1/2} \\ &\quad\times \frac{(s_\mathrm{i}-s_\mathrm{f}+m-1)}{(s_\mathrm{i}+s_\mathrm{f}-m-3)}\langle m|1\rangle_\mathrm{o}, \end{aligned} \tag{49}$$

$$\langle 1|1\rangle_{\rm o} = \left[(s_{\rm i}-1)(s_{\rm f}-1)\frac{\Gamma(2s_{\rm i})}{\Gamma^2(s_{\rm i})}\frac{\Gamma(2s_{\rm f})}{\Gamma^2(s_{\rm f})}\right]^{1/2}\frac{\Gamma^2((s_{\rm f}+s_{\rm i})/2)}{\Gamma(s_{\rm i}+s_{\rm f})}\frac{2}{(s_{\rm i}+s_{\rm f}-2)},$$

and for $s_{\rm i}, s_{\rm f} \gg 1$, the matrix elements $\langle 1|1\rangle_{\rm o}$ can be approximated by

$$\langle 1|1\rangle_{\rm o} \approx \left[2\frac{\sqrt{s_{\rm i}s_{\rm f}}}{s_{\rm i}+s_{\rm f}}\right]^{3/2}. \tag{50}$$

For the $\phi_{\rm e}(n)$ and $\phi_{\rm o}(n)$ in equations (43) and (45), the following recurrence formulas follow:

$$\begin{aligned} \phi_{\rm e}(0) &= 1,\\ \phi_{\rm e}(n+2) &= \left[\frac{(s_{\rm i}-n-2)}{(s_{\rm i}-n)}\frac{(2s_{\rm i}-n-1)(2s_{\rm i}-n)}{(n+1)(n+2)}\right]^{1/2}\phi_{\rm e}(n), \end{aligned} \tag{51}$$

and

$$\begin{aligned} \phi_{\rm o}(1) &= 1,\\ \phi_{\rm o}(n+2) &= \left[\frac{(s_{\rm i}-n-2)}{(s_{\rm i}-n)}\frac{(2s_{\rm i}-n-1)(2s_{\rm i}-n)}{(n+1)(n+2)}\right]^{1/2}\phi_{\rm o}(n). \end{aligned} \tag{52}$$

To clarify the structure of the summation terms the first few are given explicitely. The matrix elements between states with even quantum numbers assume the following form:

$$\begin{aligned} \langle m|n\rangle_{\rm e} = \langle m|0\rangle_{\rm e}\phi_{\rm e}(n)\Bigg\{ & 1 + (-1)^1\left(\frac{1}{2}\right)^1\frac{n}{1}\frac{(2s_{\rm i}-n)}{(2s_{\rm i}-1)}\\ & \times\frac{(s_{\rm f}-s_{\rm i}+2)(s_{\rm f}+s_{\rm i}-1)}{(s_{\rm f}-s_{\rm i}+2-m)(s_{\rm f}+s_{\rm i}-m-2)}\\ & + (-1)^2\left(\frac{1}{2}\right)^2\frac{n(n-2)}{1\cdot 2}\frac{(2s_{\rm i}-n)(2s_{\rm i}-n-2)}{(2s_{\rm i}-1)(2s_{\rm i}-3)}\\ & \times\frac{(s_{\rm f}-s_{\rm i}+2)(s_{\rm f}-s_{\rm i}+4)}{(s_{\rm f}-s_{\rm i}-m+2)(s_{\rm f}-s_{\rm i}-m+4)}\\ & \times\frac{(s_{\rm f}+s_{\rm i}-1)(s_{\rm f}+s_{\rm i}-3)}{(s_{\rm f}+s_{\rm i}-m-2)(s_{\rm f}+s_{\rm i}-m-4)}\\ & + (-1)^3\left(\frac{1}{2}\right)^3\frac{n(n-2)(n-4)}{1\cdot 2\cdot 3}\\ & \times\frac{(2s_{\rm i}-n)(2s_{\rm i}-n-2)(2s_{\rm i}-n-4)}{(2s_{\rm i}-1)\,(2s_{\rm i}-3)(2s_{\rm i}-5)}\\ & \times\frac{(s_{\rm f}-s_{\rm i}+2)(s_{\rm f}-s_{\rm i}+4)(s_{\rm f}-s_{\rm i}+6)}{(s_{\rm f}-s_{\rm i}-m+2)(s_{\rm f}-s_{\rm i}-m+4)(s_{\rm f}-s_{\rm i}-m+6)}\\ & \times\frac{(s_{\rm f}+s_{\rm i}-1)(s_{\rm f}+s_{\rm i}-3)(s_{\rm f}+s_{\rm i}-5)}{(s_{\rm f}+s_{\rm i}-m-2)(s_{\rm f}+s_{\rm i}-m-4)(s_{\rm f}+s_{\rm i}-m-6)} \end{aligned}$$

$$
\begin{aligned}
&+(-1)^4\left(\frac{1}{2}\right)^4\frac{n(n-2)(n-4)(n-6)}{1\cdot 2\cdot 3\cdot 4}\\
&\times\frac{(2s_\mathrm{i}-n)(2s_\mathrm{i}-n-2)(2s_\mathrm{i}-n-4)(2s_\mathrm{i}-n-6)}{(2s_\mathrm{i}-1)(2s_\mathrm{i}-3)(2s_\mathrm{i}-5)(2s_\mathrm{i}-7)}\\
&\times\frac{(s_\mathrm{f}-s_\mathrm{i}+2)(s_\mathrm{f}-s_\mathrm{i}+4)(s_\mathrm{f}-s_\mathrm{i}+6)(s_\mathrm{f}-s_\mathrm{i}+8)}{(s_\mathrm{f}-s_\mathrm{i}-m+2)(s_\mathrm{f}-s_\mathrm{i}-m+4)(s_\mathrm{f}-s_\mathrm{i}-m+6)(s_\mathrm{f}-s_\mathrm{i}-m+8)}\\
&\times\frac{(s_\mathrm{f}+s_\mathrm{i}-1)(s_\mathrm{f}+s_\mathrm{i}-3)(s_\mathrm{f}+s_\mathrm{i}-5)(s_\mathrm{f}+s_\mathrm{i}-7)}{(s_\mathrm{f}+s_\mathrm{i}-m-2)(s_\mathrm{f}+s_\mathrm{i}-m-4)(s_\mathrm{f}+s_\mathrm{i}-m-6)(s_\mathrm{f}+s_\mathrm{i}-m-8)}\\
&+\cdots+(-1)^{n/2-1}\left(\frac{1}{2}\right)^{n/2-1}\frac{n!}{(n/2-1)!}\cdots\Bigg\}. \qquad (53)
\end{aligned}
$$

For the matrix elements between states with odd quantum numbers, the following terms are obtained:

$$
\begin{aligned}
\langle m|n\rangle_\mathrm{o} = \langle m|1\rangle_\mathrm{o}\phi_\mathrm{o}(n)\Bigg\{&1+(-1)^1\left(\frac{1}{2}\right)^1\frac{(n-1)}{1}\frac{(2s_\mathrm{i}-n-1)}{(2s_\mathrm{i}-1)}\\
&\times\frac{(s_\mathrm{f}-s_\mathrm{i}+2)}{(s_\mathrm{f}-s_\mathrm{i}-m+3)}\frac{(s_\mathrm{f}+s_\mathrm{i}-1)}{(s_\mathrm{f}+s_\mathrm{i}-m-3)}\\
&+(-1)^2\left(\frac{1}{2}\right)^2\frac{(n-1)(n-3)}{1\cdot 2}\frac{(2s_\mathrm{i}-n-1)(2s_\mathrm{i}-n-3)}{(2s_\mathrm{i}-1)(2s_\mathrm{i}-3)}\\
&\times\frac{(s_\mathrm{f}-s_\mathrm{i}+2)(s_\mathrm{f}-s_\mathrm{i}+4)}{(s_\mathrm{f}-s_\mathrm{i}-m+3)(s_\mathrm{f}-s_\mathrm{i}-m+5)}\\
&\times\frac{(s_\mathrm{f}+s_\mathrm{i}-1)(s_\mathrm{f}+s_\mathrm{i}-3)}{(s_\mathrm{f}+s_\mathrm{i}-m-3)(s_\mathrm{f}+s_\mathrm{i}-m-5)}\\
&+(-1)^3\left(\frac{1}{2}\right)^3\frac{(n-1)(n-3)(n-5)}{1\cdot 2\cdot 3}\\
&\times\frac{(2s_\mathrm{i}-n-1)(2s_\mathrm{i}-n-3)(2s_\mathrm{i}-n-5)}{(2s_\mathrm{i}-1)(2s_\mathrm{i}-3)(2s_\mathrm{i}-5)}\\
&\times\frac{(s_\mathrm{f}-s_\mathrm{i}+2)(s_\mathrm{f}-s_\mathrm{i}+4)(s_\mathrm{f}-s_\mathrm{i}+6)}{(s_\mathrm{f}-s_\mathrm{i}-m+3)(s_\mathrm{f}-s_\mathrm{i}-m+5)(s_\mathrm{f}-s_\mathrm{i}-m+7)}\\
&\times\frac{(s_\mathrm{f}+s_\mathrm{i}-1)(s_\mathrm{f}+s_\mathrm{i}-3)(s_\mathrm{f}+s_\mathrm{i}-5)}{(s_\mathrm{f}+s_\mathrm{i}-m-3)(s_\mathrm{f}+s_\mathrm{i}-m-5)(s_\mathrm{f}+s_\mathrm{i}-m-7)}\\
&+\cdots+(-1)^{(n-1)/2-1}\left(\frac{1}{2}\right)^{(n-1)/2-1}\cdots\Bigg\}. \qquad (54)
\end{aligned}
$$

In appendix A, the exact matrix elements are explicitely given for $n = 2$–7.

In a next step, it is tried to find an approximate solution for the exact results of equations (41) and (42) and especially a closed form expression when $s_\mathrm{i} \gg n$. The terms within the summation in equation (41) can be separated into an exact part $\Pi(l)$ which allows no simplification and an approximatable part $\sigma_\mathrm{e}(l)$ which consists of five

Gamma functions. Instead of the exact expression, the asymptotic forms are inserted, where for $a \gg 1$ and $\varepsilon \ll a$ the relation

$$\Gamma(a+\varepsilon) \approx \Gamma(a)a^{\varepsilon}\mathrm{e}^{(\varepsilon/a)(\varepsilon-1/2)} \approx \Gamma(a)a^{\varepsilon} \tag{55}$$

is applied, so that one obtains

$$\sum_{\mathrm{e}} = \sum_{l=0}^{n/2} \Pi_{\mathrm{e}}(l)\sigma_{\mathrm{e}}(l) \approx \sigma_{\mathrm{e},0} \sum_{l=0}^{n/2} \left(\frac{1}{2}\right)^{2l} \Pi_{\mathrm{e}}(l)\lambda_{\mathrm{e}}^{l}, \tag{56}$$

$$\Pi_{\mathrm{e}}(l) = \frac{(-1)^{l}2^{2l}\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+l)}{l!(n/2-l)!\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2+1+l)}, \tag{57}$$

$$\sigma_{\mathrm{e}}(l) = \frac{\Gamma(2s_{\mathrm{i}}-2l)\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-m/2-l)}{\Gamma(s_{\mathrm{i}}-n/2-l+1)\Gamma(s_{\mathrm{i}}-l)\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2-l)}, \tag{58}$$

where λ_{e} shows the following parameter dependence:

$$\lambda_{\mathrm{e}} = \frac{(s_{\mathrm{i}}-n/2+1)(s_{\mathrm{f}}+s_{\mathrm{i}}+1)}{s_{\mathrm{i}}(s_{\mathrm{f}}+s_{\mathrm{i}}-m)}, \tag{59}$$

and the summation index l independent form of $\sigma_{\mathrm{e}}(l)$ yields

$$\sigma_{\mathrm{e},0} = \frac{\Gamma(2s_{\mathrm{i}})\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-m/2)}{\Gamma(s_{\mathrm{i}})\Gamma(s_{\mathrm{i}}-n/2+1)\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2)}. \tag{60}$$

Thus the summation in equation (56) yields

$$\sum_{\mathrm{e}} = \sigma_{\mathrm{e},0} \sum_{l=0}^{n/2} \frac{(-1)^{l}\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+l)}{l!(n/2-l)!\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2+1+l)}\lambda_{\mathrm{e}}^{l}. \tag{61}$$

This summation can be set in relation to the Jacobi polynomials [1, p. 775, no. 22.3.2]

$$\sum_{\mathrm{e}} = \sigma_{\mathrm{e},0}\frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-(m-n)/2+1)} P_{n/2}^{(s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2,(m-n)/2}(1-2\lambda_{\mathrm{e}}). \tag{62}$$

Substitution of the Jacobi polynomials by the hypergeometric function [1, p. 561, no. 15.4.6]

$$P_{n'}^{\alpha,\beta}(1-2x) = \frac{\Gamma(\alpha+n'+1)}{n'!\Gamma(\alpha+1)}{}_2F_1(-n',\alpha+\beta+n'+1;\alpha+1;x) \tag{63}$$

leads to

$$\sum_{\mathrm{e}} = \sigma_{\mathrm{e},0}\frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1)}{(n/2)!\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2+1)} \times {}_2F_1\left(-\frac{n}{2}, \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}+1; \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}-\frac{m}{2}+1; \lambda_{\mathrm{e}}\right). \tag{64}$$

Finally, inserting equation (64) into equation (41) leads to the following approximate solution:

$$\langle m|n\rangle_{\mathrm{e}} \approx \langle m|0\rangle_{\mathrm{e}}\phi_{\mathrm{e}}(n) \times {}_2F_1\left(-\frac{n}{2}, \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}+1; \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}-\frac{m}{2}+1; \lambda_{\mathrm{e}}\right), \quad s_{\mathrm{i}} \gg \frac{n}{2}. \tag{65}$$

A similar treatment for matrix elements with odd quantum numbers leads to

$$\sum_{\mathrm{o}} = \sum_{l=0}^{(n-1)/2} \Pi_{\mathrm{o}}(l)\sigma_{\mathrm{o}}(l) \approx \sigma_{\mathrm{o},0} \sum_{l=0}^{(n-1)/2} \left(\frac{1}{2}\right)^{2l} \Pi_{\mathrm{o}}(l)\lambda_{\mathrm{o}}^{l}, \tag{66}$$

$$\Pi_{\mathrm{o}}(l) = \frac{(-1)^l 2^{2l}\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1+l)}{l!((n-1)/2-l)!\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-(m-1)/2+1+l)}, \tag{67}$$

$$\sigma_{\mathrm{o}}(l) = \frac{\Gamma(2s_{\mathrm{i}}-2l)\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-(m-1)/2-1-l)}{\Gamma(s_{\mathrm{i}}-(n-1)/2-l)\Gamma(s_{\mathrm{i}}-l)\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2-l)}, \tag{68}$$

$$\lambda_{\mathrm{o}} = \frac{(s_{\mathrm{i}}-(n-1)/2)(s_{\mathrm{f}}+s_{\mathrm{i}}+1)}{s_{\mathrm{i}}(s_{\mathrm{f}}+s_{\mathrm{i}}-m-1)}, \tag{69}$$

$$\sigma_{\mathrm{o},0} = \frac{\Gamma(2s_{\mathrm{i}})\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2-(m-1)/2-1)}{\Gamma(s_{\mathrm{i}})\Gamma(s_{\mathrm{i}}-(n-1)/2)\Gamma((s_{\mathrm{f}}+s_{\mathrm{i}})/2+1/2)}. \tag{70}$$

After rearranging and inserting equation (66) into equation (42), the approximate solution for the odd matrix elements is obtained as follows:

$$\sum_{\mathrm{o}} = \sigma_{\mathrm{o},0}\frac{((n-1)/2)!\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-(m-n)/2+1)} P_{(n-1)/2}^{(s_{\mathrm{f}}-s_{\mathrm{i}})/2-(m-1)/2,(m-n)/2}(1-2\lambda_{\mathrm{o}}), \tag{71}$$

$$\langle m|n\rangle_{\mathrm{o}} \approx \langle m|1\rangle_{\mathrm{o}}\phi_{\mathrm{o}}(n) \times {}_2F_1\left(-\frac{n-1}{2}, \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}+1; \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}-\frac{m-1}{2}+1; \lambda_{\mathrm{o}}\right). \tag{72}$$

A closer analysis of equations (65) and (72) shows that still a further useful simplification is possible. Assuming $m \ll s_{\mathrm{f}}$ and $s_{\mathrm{f}} \gg 1$ one obtains for λ_{e} and λ_{o} approximately the values $\lambda_{\mathrm{e}} = \lambda_{\mathrm{o}} \approx 1$. As a consequence, the expression for the hypergeometric function can be approximated using formula 15.1.20 of AS [1, p. 556]:

$${}_2F_1\left(-\frac{n}{2}, \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}+1; \frac{s_{\mathrm{f}}-s_{\mathrm{i}}}{2}-\frac{m}{2}+1; \lambda_{\mathrm{e}}\right) \approx (-1)^{n/2}\frac{(m/2)!}{((m-n)/2)!}\frac{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2-m/2+1)}{\Gamma((s_{\mathrm{f}}-s_{\mathrm{i}})/2+1-(m-n)/2)}, \tag{73}$$

$$
\begin{aligned}
&{}_2F_1\left(-\frac{n-1}{2}, \frac{s_\mathrm{f}-s_\mathrm{i}}{2}+1; \frac{s_\mathrm{f}-s_\mathrm{i}}{2}-\frac{m-1}{2}+1; \lambda_\mathrm{o}\right) \\
&\quad\approx (-1)^{(n-1)/2}\frac{((m-1)/2)!}{((m-n)/2)!}\frac{\Gamma((s_\mathrm{f}-s_\mathrm{i})/2-(m-1)/2+1)}{\Gamma((s_\mathrm{f}-s_\mathrm{i})/2+1-(m-n)/2)}, \\
&s_\mathrm{i}, s_\mathrm{f} \gg 1,\ s_\mathrm{i} \gg n,\ s_\mathrm{f} \gg m.
\end{aligned}
\tag{74}
$$

In equations (73) and (74), the asymptotic forms of the summations in the exact expressions of equations (41) and (42) are introduced. However, by additional approximations of the prefactors $\langle m|1\rangle$, $\langle m|0\rangle$, $\Phi_\mathrm{e}(n)$, and $\Phi_\mathrm{o}(n)$ one obtains a very comfortable form for the Rosen–Morse matrix elements for small quantum numbers:

$$
\begin{aligned}
\langle m|n\rangle_\mathrm{e} \approx{}& \langle 0|0\rangle_\mathrm{e}\Gamma\left(\frac{s_\mathrm{f}-s_\mathrm{i}}{2}+1\right)(-1)^{(n+m)/2}\sqrt{\frac{m!}{n!}}\,2^{n/2} \\
&\times \frac{1}{((m-n)/2)!\Gamma((s_\mathrm{f}-s_\mathrm{i})/2+1-(m-n)/2)}\frac{s_\mathrm{i}^{n/2}}{(s_\mathrm{f}+s_\mathrm{i})^{m/2}},
\end{aligned}
\tag{75}
$$

$$
\begin{aligned}
\langle m|n\rangle_\mathrm{o} \approx{}& \langle 1|1\rangle_\mathrm{o}\Gamma\left(\frac{s_\mathrm{f}-s_\mathrm{i}}{2}+1\right)(-1)^{(n+m)/2-1}\sqrt{\frac{m!}{n!}}\,2^{(n-1)/2} \\
&\times \frac{1}{((m-n)/2)!\Gamma((s_\mathrm{f}-s_\mathrm{i})/2+1-(m-n)/2)}\frac{s_\mathrm{i}^{(n-1)/2}}{(s_\mathrm{f}+s_\mathrm{i})^{(m-1)/2}}, \\
&s_\mathrm{i}, s_\mathrm{f} \gg 1,\ s_\mathrm{f} \gg m,\ s_\mathrm{i} \gg n,\ m \geqslant n,
\end{aligned}
\tag{76}
$$

with the recurrence relations equally valid for even and odd quantum numbers:

$$
\langle m|n+2\rangle = -\frac{(m-n)}{\sqrt{(n+1)(n+2)}}\;\frac{2s_\mathrm{i}}{(s_\mathrm{f}-s_\mathrm{i}-m+n+2)}\langle m|n\rangle, \tag{77}
$$

$$
\langle m+2|n\rangle = -\frac{\sqrt{(m+1)(m+2)}}{(m-n+2)}\frac{(s_\mathrm{f}-s_\mathrm{i}-m+n)}{(s_\mathrm{f}+s_\mathrm{i})}\langle m|n\rangle, \tag{78}
$$

$$
\langle m+2|m+2\rangle = \frac{2s_\mathrm{i}-m}{s_\mathrm{f}+s_\mathrm{i}-m-1}\langle m|m\rangle. \tag{79}
$$

The approximations in equations (75) and (76) are only tolerable for very low quantum numbers. Thus the significance of these expressions lies mainly in the very clear asymptotic parameter dependences and hardly in the numerical relevance, as for low quantum numbers the exact solutions are superior.

3. Conclusions

In this study exact analytical expressions for matrix elements and Franck–Condon factors, respectively, have been developed for the modified Pöschl–Teller oscillator. The numerically extremely instable double summation has been replaced by a simple summation. As a consequence, the total set of matrix elements with quantum numbers defined by the complete basis set of the bound states can now be calculated.

Approximate solutions which are satisfied for most cases of the molecular parameters has allowed to find analytical closed form expressions without any further summation. Thus the parameter dependence can be analyzed very clearly.

Appendix A

The explicite exact expressions for the matrix elements with occupation numbers $n = 0$–7 are given. One starts from equation (43) for even matrix elements:

$$\langle m|n\rangle_{\mathrm{e}} = \langle m|0\rangle_{\mathrm{e}}\phi_{\mathrm{e}}(n)F_{\mathrm{e}}(n,m), \qquad F_{\mathrm{e}}(n,m) = \sum_{l=0}^{n/2} S_{\mathrm{e}}(l). \tag{A.1}$$

$$F_{\mathrm{e}}(0,m) = 1, \tag{A.2}$$

$$F_{\mathrm{e}}(2,m) = 1 - 2\frac{(s_{\mathrm{i}}-1)}{(2s_{\mathrm{i}}-1)}\frac{(s_{\mathrm{f}}-s_{\mathrm{i}}+2)(s_{\mathrm{f}}+s_{\mathrm{i}}-1)}{(s_{\mathrm{f}}-s_{\mathrm{i}}-m+2)(s_{\mathrm{f}}+s_{\mathrm{i}}-m-2)}, \tag{A.3}$$

$$\begin{aligned} F_{\mathrm{e}}(4,m) = 1 &- 4\frac{(s_{\mathrm{i}}-2)}{(2s_{\mathrm{i}}-1)}\frac{(s_{\mathrm{f}}-s_{\mathrm{i}}+2)(s_{\mathrm{f}}+s_{\mathrm{i}}-1)}{(s_{\mathrm{f}}-s_{\mathrm{i}}-m+2)(s_{\mathrm{f}}+s_{\mathrm{i}}-m-2)} \\ &+ 4\frac{(s_{\mathrm{i}}-2)(s_{\mathrm{i}}-3)}{(2s_{\mathrm{i}}-1)(2s_{\mathrm{i}}-3)}\frac{(s_{\mathrm{f}}-s_{\mathrm{i}}+2)(s_{\mathrm{f}}-s_{\mathrm{i}}+4)}{(s_{\mathrm{f}}-s_{\mathrm{i}}-m+2)(s_{\mathrm{f}}-s_{\mathrm{i}}-m+4)} \\ &\times \frac{(s_{\mathrm{f}}+s_{\mathrm{i}}-1)(s_{\mathrm{f}}+s_{\mathrm{i}}-3)}{(s_{\mathrm{f}}+s_{\mathrm{i}}-m-2)(s_{\mathrm{f}}+s_{\mathrm{i}}-m-4)}, \end{aligned} \tag{A.4}$$

$$\begin{aligned} F_{\mathrm{e}}(6,m) = 1 &- 6\frac{(s_{\mathrm{i}}-3)}{(2s_{\mathrm{i}}-1)}\frac{(s_{\mathrm{f}}-s_{\mathrm{i}}+2)(s_{\mathrm{f}}+s_{\mathrm{i}}-1)}{(s_{\mathrm{f}}-s_{\mathrm{i}}-m+2)(s_{\mathrm{f}}+s_{\mathrm{i}}-m-2)} \\ &+ 12\frac{(s_{\mathrm{i}}-3)(s_{\mathrm{i}}-4)}{(2s_{\mathrm{i}}-1)(2s_{\mathrm{i}}-3)}\frac{(s_{\mathrm{f}}-s_{\mathrm{i}}+2)(s_{\mathrm{f}}-s_{\mathrm{i}}+4)}{(s_{\mathrm{f}}-s_{\mathrm{i}}-m+2)(s_{\mathrm{f}}-s_{\mathrm{i}}-m+4)} \\ &\times \frac{(s_{\mathrm{f}}+s_{\mathrm{i}}-1)(s_{\mathrm{f}}+s_{\mathrm{i}}-3)}{(s_{\mathrm{f}}+s_{\mathrm{i}}-m-2)(s_{\mathrm{f}}+s_{\mathrm{i}}-m-4)} \\ &- 8\frac{(s_{\mathrm{i}}-3)(s_{\mathrm{i}}-4)(s_{\mathrm{i}}-5)}{(2s_{\mathrm{i}}-1)(2s_{\mathrm{i}}-3)(2s_{\mathrm{i}}-5)} \\ &\times \frac{(s_{\mathrm{f}}-s_{\mathrm{i}}+2)(s_{\mathrm{f}}-s_{\mathrm{i}}+4)(s_{\mathrm{f}}-s_{\mathrm{i}}+6)}{(s_{\mathrm{f}}-s_{\mathrm{i}}-m+2)(s_{\mathrm{f}}-s_{\mathrm{i}}-m+4)(s_{\mathrm{f}}-s_{\mathrm{i}}-m+6)} \\ &\times \frac{(s_{\mathrm{f}}+s_{\mathrm{i}}-1)(s_{\mathrm{f}}+s_{\mathrm{i}}-3)(s_{\mathrm{f}}+s_{\mathrm{i}}-5)}{(s_{\mathrm{f}}+s_{\mathrm{i}}-m-2)(s_{\mathrm{f}}+s_{\mathrm{i}}-m-4)(s_{\mathrm{f}}+s_{\mathrm{i}}-m-6)}. \end{aligned} \tag{A.5}$$

For odd matrix elements, one starts from equation (45):

$$\langle m|n\rangle_{\mathrm{o}} = \langle m|1\rangle_{\mathrm{o}}\phi_{\mathrm{o}}(n)F_{\mathrm{o}}(n,m), \qquad F_{\mathrm{o}}(n,m) = \sum_{l=0}^{(n-1)/2} S_{\mathrm{o}}(l). \tag{A.6}$$

$$F_o(1,m) = 1, \tag{A.7}$$

$$F_o(3,m) = 1 - 2\frac{(s_i-2)}{(2s_i-1)}\frac{(s_f-s_i+2)(s_f+s_i+1)}{(s_f-s_i-m+3)(s_f+s_i-m-3)}, \tag{A.8}$$

$$\begin{aligned} F_o(5,m) = 1 &- 4\frac{(s_i-3)}{(2s_i-1)}\frac{(s_f-s_i+2)(s_f+s_i-1)}{(s_f-s_i-m+3)(s_f+s_i-m-3)} \\ &+ 4\frac{(s_i-3)(s_i-4)}{(2s_i-1)(2s_i-3)}\frac{(s_f-s_i+2)(s_f-s_i+4)}{(s_f-s_i-m+3)(s_f-s_i-m+5)} \\ &\times \frac{(s_f+s_i-1)(s_f+s_i-3)}{(s_f+s_i-m-3)(s_f+s_i-m-5)}, \end{aligned} \tag{A.9}$$

$$\begin{aligned} F_o(7,m) = 1 &- 6\frac{(s_i-4)}{(2s_i-1)}\frac{(s_f-s_i+2)(s_f+s_i-1)}{(s_f-s_i-m+3)(s_f+s_i-m-3)} \\ &+ 12\frac{(s_i-4)(s_i-5)}{(2s_i-1)(2s_i-3)}\frac{(s_f-s_i+2)(s_f-s_i+4)}{(s_f-s_i-m+3)(s_f-s_i-m+5)} \\ &\times \frac{(s_f+s_i-1)(s_f+s_i-3)}{(s_f+s_i-m-3)(s_f+s_i-m-5)} \\ &- 8\frac{(s_i-4)(s_i-5)(s_i-6)}{(2s_i-1)(2s_i-3)(2s_i-5)} \\ &\times \frac{(s_f-s_i+2)(s_f-s_i+4)(s_f-s_i+6)}{(s_f-s_i-m+3)(s_f-s_i-m+5)(s_f-s_i-m+7)} \\ &\times \frac{(s_f+s_i-1)(s_f+s_i-3)(s_f+s_i-5)}{(s_f+s_i-m-3)(s_f+s_i-m-5)(s_f+s_i-m-7)}. \end{aligned} \tag{A.10}$$

Appendix B

For the special case $s_f = s_i$, one finds the following exclusion principles for matrix elements with even and odd quantum numbers:

$$\langle m|n\rangle_{e,o} = \delta_{n,m}. \tag{B.1}$$

Another special case exists if the arguments of the Gamma functions in the denominators of equations (41) and (42) are negative integers

$$m_e = \frac{s_f - s_i}{2} - \frac{m}{2} + 1 + l = 0, -1, -2, \ldots, \tag{B.2}$$

$$m_o = \frac{s_f - s_i}{2} - \frac{m-1}{2} + 1 + l = 0, -1, -2, \ldots. \tag{B.3}$$

This can only be the case if $(s_f - s_i)/2$ is an integer. As the experimental value is not known better than some 10^{-3} cm^{-1}, one can simply introduce a small difference in the frequencies and s_i, s_f, respectively, to avoid accidental numerical instabilities.

The exact treatment yields further selection rules for even and odd quantum numbers n and m.

If M is a positive integer,

$$M = \frac{s_\mathrm{f} - s_\mathrm{i}}{2} > 0, \tag{B.4}$$

then the restriction

$$\frac{m-n}{2} < M + 1 \tag{B.5}$$

implies that

$$\langle m|n\rangle_{\mathrm{e,o}} \neq 0, \tag{B.6}$$

else that

$$\langle m|n\rangle_{\mathrm{e,o}} = 0. \tag{B.7}$$

If, however, M is a negative integer,

$$M = \frac{s_\mathrm{f} - s_\mathrm{i}}{2} < 0, \tag{B.8}$$

then the condition

$$\frac{m-n}{2} > M - 1 \tag{B.9}$$

implies that

$$\langle m|n\rangle_{\mathrm{e,o}} \neq 0, \tag{B.10}$$

else that

$$\langle m|n\rangle_{\mathrm{e,o}} = 0. \tag{B.11}$$

References

[1] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions* (Wiley, New York, 1970).
[2] H. Ahmedov and I.H. Duru, J. Phys. A 30 (1997) 173.
[3] A.O. Barut and H. Beker, Europhys. Lett. 14 (1991) 197.
[4] A.O. Barut and A. Inomata, International Atomic Agency, Miramare–Trieste, IC/87/2,3 (January 1987).
[5] A.O. Barut and A. Inomata and R. Wilson, J. Phys. A 20 (1987) 4083.
[6] M. Böhm and G. Junker, J. Math. Phys. 28 (1987) 1978.
[7] C. Brif, A. Vourdas and A. Mann, J. Phys. A 29 (1996) 5873.
[8] L.V. Chebotarev, J. Phys. A 29 (1996) 1465.
[9] Y.S. Choi and C.B. Moore, J. Chem. Phys. 110 (1993) 1111.
[10] C. Daskaloyannis, J. Phys. A 25 (1992) 2261.
[11] M.J. Englefield, J. Math. Phys. 28 (1987) 827.
[12] S. Flügge, *Rechenmethoden der Quantenmechanik* (Springer, Berlin, 1993).
[13] A. Frank and K.B. Wolf, J. Math. Phys. 26 (1985) 973.
[14] T. Fukui, Phys. Lett. A 178 (1993) 1.
[15] J. Ge and J.Z.H. Zhang, J. Chem. Phys. 105 (1996) 8628.

[16] I.S. Gradshteyn and I.M. Ryzhik, *Table of Integrals, Series and Products* (Academic Press, New York, 1980).
[17] C. Grosche, Ann. Phys. 201 (1990) 258; 204 (1990) 208; 187 (1988) 110.
[18] C. Grosche, J. Phys. A 22 (1989) 5073; 23 (1990) 4885.
[19] C. Grosche, Fortschr. Phys. 38 (1990) 531.
[20] C. Grosche, Desy 95-099 (May 1995); 89-049 (April 1989).
[21] M.E. Grypeos, G.A. Lalazissis, S.E. Massen and C.P. Panos, J. Phys. G 17 (1991) 1093.
[22] H. Hornburger and G.H.F. Diercksen, to be published.
[23] H. Hornburger and M. Melzig, Z. Phys. D, under revision.
[24] H. Hornburger, K.D. Reinsch, M. Melzig and S. Leach, Z. Phys. D 5 (1987) 151.
[25] L. Infeld and T.E. Hull, Rev. Modern Phys. 23 (1951) 21.
[26] G. Junker and M. Böhm, Phys. Lett. A 117 (1986) 375.
[27] Y. Kakiuti and T. Shimanouchi, J. Chem. Phys. 25 (1956) 1252.
[28] H. Kleinert and I. Mustapic, J. Math. Phys. 33 (1992) 643.
[29] C.G. Koutroulos, J. Phys. G 17 (1991) 1069.
[30] P.M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953).
[31] M.M. Nieto, Phys. Rev. A 17 (1978) 1273.
[32] D. Pertsch, J. Phys. A 23 (1990) 4145.
[33] G. Pöschl and E. Teller, Z. Phys. 83 (1933) 143.
[34] P. Pulay, G. Fogarasi and J.E. Boggs, J. Chem. Phys. 74 (1981) 3999.
[35] C. Quesne, J. Phys. A 21 (1988) 4487; 22 (1989) 3723.
[36] N. Rosen and P.M. Morse, Phys. Rev. 42 (1932) 210.
[37] O.P. Shadrin and N.I. Zhirnov, Opt. Spectr. 38 (1975) 367.
[38] Y. Wu, J. Math. Phys. 31 (1990) 2586.
[39] J. Zuniga, M. Alacid, A. Requena and A. Bastida, Int. J. Quantum Chem. 57 (1996) 43.