Jahn-Teller E-e Problem: Diagonalization by Means of a Transformed Basis

M. Birkhold and M. Wagner
Institut für Theoretische Physik, Universität Stuttgart

Z. Naturforsch. **34a**, 667–671 (1979); received April 28, 1979

A unitary transformation is applied to the $E-e$ Jahn-Teller problem. The eigenfunctions of the diagonal part of the transformed Hamiltonian are utilized for a Ritz diagonalization procedure. Results are given for basic sets of 12, 20 and 42 functions and compared with the respective conventional calculations. In the transformed picture the exact results are approached in a different manner than in the original one and thus the reliability of the numerical work is improved.

1. Introduction

In dynamical Jahn-Teller (J.T.) systems the conventional Born-Oppenheimer approximation breaks down and a non-adiabatic calculation has to be done. Numerical efforts in this direction have been undertaken by Longuet-Higgins [1], Uehara [2] and others. In these approaches the non-adiabatic Hamiltonian is projected onto the eigenbasis of the decoupled part of the total Hamiltonian. The secular equation then is solved numerically. However, calculations of this kind only lead to a restricted physical insight. It is therefore highly desirable to study analytical approaches.

Furthermore, the Jahn-Teller problem has the peculiarity that in the strong coupling limit energetically far-distant states ($\sim \varkappa^2$) remain coupled, if the eigenbasis of the decoupled Hamiltonian is chosen for the numerical procedure. Hence, if the number of basis functions is not chosen exceedingly high, there is some uncertainty about the results. Therefore, there is a need for numerical results which follow from the use of an alternative choice of basis.

One of us (Wagner [3]) has shown that by means of an exponential transformation the Hamiltonian H can be brought to a form of improved diagonality H. In this paper we will employ this transformation for a definition of a modified set of basis functions to be used in a diagonalization procedure. It is the purpose of this paper to compare these results with those found by means of the conventional basis. Several different choices are made for the number of functions in the respective basic sequences. We calculate the energy levels and the Ham factors for the $E-e$ system.

2. The Jahn-Teller $E-e$ system

We confine ourselves to the linear $E-e$ J.-T. case, which is found in a trigonal or hexagonal surrounding. Here a doubly degenerate electronic state interacts with a doubly degenerate vibrational mode. The Hamiltonian reads ($\hbar = 1$) *

$$\begin{aligned} H = {} & \Omega (a_1^+ a_1 + a_2^+ a_2) + \omega (b_1^+ b_1 + b_2^+ b_2) \\ & + \varkappa \{(a_1^+ a_1 - a_2^+ a_2)(b_2 + b_2^+) \\ & + (a_1^+ a_2 + a_2^+ a_1)(b_1 + b_1^+)\} . \end{aligned} \tag{1}$$

The b_i^+, b_i are oscillator creation and annihilation operators, whereas the a_i^+, a_i may be taken as either electronic or excitonic creation and annihilation operators. Ω is the electron and ω the phonon energy. $\varkappa$ is the electron phonon coupling parameter with the dimension of an energy. The electron dynamics of this $E-e$ J.-T. system is characterized by an SU(2) algebra, which can be completely described by the following Hermitian operators:

$$\begin{aligned} A &= a_1^+ a_1 + a_2^+ a_2 = 1 , \\ B &= a_1^+ a_1 - a_2^+ a_2 , \\ C &= a_1^+ a_2 + a_2^+ a_1 , \\ D &= i (a_1^+ a_2 - a_2^+ a_1) . \end{aligned} \tag{2a–d}$$

3. Nonlinear Canonical Transformation

In earlier work [3] it has been found that the $E-e$ Jahn-Teller Hamiltonian may be made "more

Reprint requests to Prof. M. Wagner, Institut für Theoretische Physik, Universität Stuttgart, Pfaffenwaldring 57, D-7000 Stuttgart 80.

0340-4811 / 79 / 0600-0667 $ 01.00/0

* In contrast to the notation of Wagner [3] the indices for the b-operators have been interchanged. This, in view of group-theoretical transformations, is the correct notation, but is of no relevance in our calculations.

diagonal" by means of a unitary exponential transformation of the form

$$U = e^{\lambda S}, \quad S = (a_1^+ a_1 - a_2^+ a_2)(b_2 - b_2^+) + (a_1^+ a_2 + a_2^+ a_1)(b_1 - b_1^+),$$
$$\lambda = \varkappa/\omega . \tag{3}$$

The transformed Hamiltonian can be written in the closed form [3]

$$U^{-1} H U \equiv \tilde{H} = (\Omega - \omega \lambda^2)(a_1^+ a_1 + a_2^+ a_2) + \omega (b_1^+ b_1 + b_2^+ b_2) + \tilde{H}_{\text{nd}} \tag{4}$$

with

$$\tilde{H}_{\text{nd}} = 4\omega\lambda^3 \sum_{n=0}^{\infty} \frac{(4\lambda^2)^n (\beta^2+\gamma^2)^n}{(2n+3)!} \cdot (2n+2)(S - 2T) - 2\omega\lambda^2 \sum_{n=0}^{\infty} \frac{(4\lambda^2)^n(\beta^2+\gamma^2)^n}{(2n+2)!} \cdot (2n+1)(A + 2U), \tag{5}$$

$$U = i D (b_1^+ b_2 - b_2^+ b_1), \tag{6a}$$
$$T = (B\gamma - C\beta)(b_1^+ b_2 - b_2^+ b_1), \tag{6b}$$
$$\beta = b_2 - b_2^+, \quad \gamma = b_1 - b_1^+ . \tag{6c}$$

We choose the eigenfunctions of the diagonal part of $\tilde{H}$ as the basis for a Ritz variational procedure,

$$\tilde{\varphi}^i_{n_1, n_2} = a_i^+ \frac{(b_1^+)^{n_1} (b_2^+)^{n_2}}{\sqrt{n_1!}\sqrt{n_2!}} \cdot |0\rangle = |i; n_1, n_2\rangle, \quad i = 1, 2, \quad n_j = 0, 1, 2, 3, \ldots . \tag{7}$$

This leads to the secular equation for the eigenvalues E of the Hamiltonian (4):

$$\det[\tilde{H}^{i,j}_{n_1, n_2, m_1, m_2} - E \cdot \delta_{ij} \cdot \delta_{n_1, m_1} \cdot \delta_{n_2, m_2}] = 0, \tag{8}$$

where $\tilde{H}^{ij}_{n_1, n_2, m_1, m_2}$ are the matrix elements

$$\langle i; n_1, n_2 | H | j; m_1, m_2 \rangle ;$$

their evaluation is given in Appendix A. To approximate the exact solution we successively use different finite sets of basis functions. Simultaneously we calculate the problem in the original picture, as done by Longuet-Higgins, with respectively the same number of basis functions as in the transformed space. The numerical results of both treatments are drawn in Figs. 1 to 5.

4. Ham factors

Let us denote the lowest two eigenfunctions by ψ_1 and ψ_2. They are doubly degenerate and in the transformed space they are given by

$$\tilde{\psi}_1 = (\exp \lambda S)\, \psi_1, \quad \tilde{\psi}_2 = (\exp \lambda S)\, \psi_2 .$$

By definition the Ham (Ham [4]) factors are given by

$$q = \langle \psi_1 | B | \psi_1 \rangle = \langle \tilde{\psi}_1 | \tilde{B} | \tilde{\psi}_1 \rangle, \tag{9a}$$
$$p = i \langle \psi_2 | D | \psi_1 \rangle = i \langle \tilde{\psi}_2 | D | \tilde{\psi}_1 \rangle, \tag{9b}$$

where

$$\tilde{B} = e^{-\lambda S} B e^{\lambda S} = B + \frac{B\gamma^2 - C\beta\gamma}{\beta^2+\gamma^2} \cdot (\cosh 2x - 1) - i \frac{D\gamma}{\sqrt{\beta^2+\gamma^2}} \sinh 2x ,$$

$$\tilde{C} = e^{-\lambda S} C e^{\lambda S} = C + \frac{C\beta^2 - B\beta\gamma}{\beta^2+\gamma^2} \cdot (\cosh 2x - 1) + i \frac{D\beta}{\sqrt{\beta^2+\gamma^2}} \sinh 2x ,$$

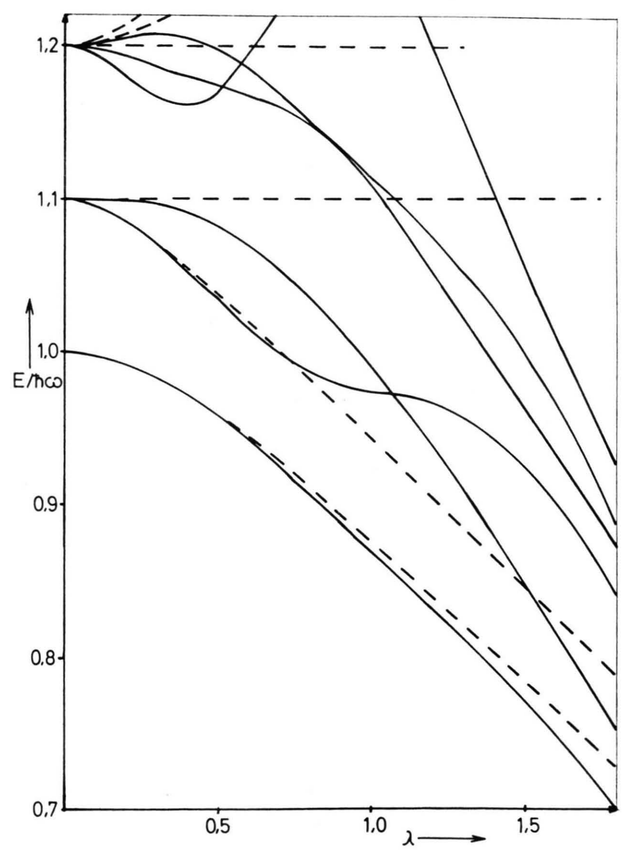

Fig. 1. Eigenvalues of the E-e-problem. $\lambda = \varkappa/\omega$ is the coupling strength. Diagonalization with a basic sequence of 12 functions. ----- original picture, —— transformed picture.

$$\tilde{D} = e^{-\lambda S} D e^{\lambda S} = D \cosh 2x + i \frac{B\gamma - C\beta}{\sqrt{\beta^2+\gamma^2}} \sinh 2x \,,$$

$$x = \lambda \sqrt{\beta^2+\gamma^2} \,. \tag{10}$$

Computations may be checked by the exact relation (Ham [4])

$$2q - p = 1 \,. \tag{11}$$

We have established our variational procedure in such a manner that both the eigenvalues and eigenvectors of H and $\tilde{H}$ are evaluated simultaneously. It is thus straightforward to calculate also the Ham factors. The results are given in Figure 6. We mention that the Ham factors as calculated with the 2 "bare" ground-state wave-functions of the diagonal part of the transformed Hamiltonian (4) have been given in an earlier communication (Sigmund, Wagner, Birkhold [5]).

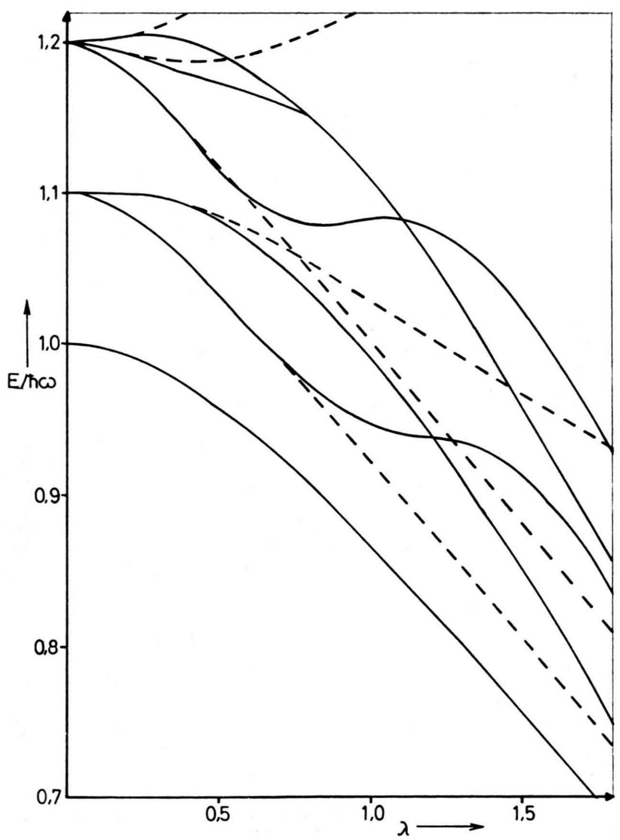

Fig. 2. Eigenvalues of the E–e-problem. $\lambda = \varkappa/\omega$ is the coupling strength. Diagonalization with a basic sequence of 20 functions. ----- original picture, ——— transformed picture.

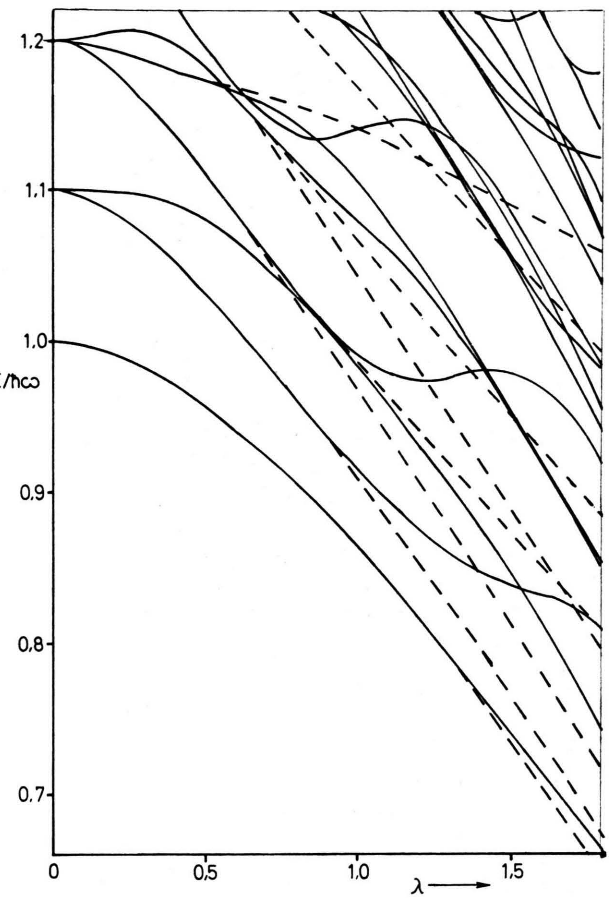

Fig. 3. Eigenvalue of the E–e-problem. $\lambda = \varkappa/\omega$ is the coupling strength. Diagonalization with a basic sequence of 42 functions. ----- original picture, ——— transformed picture.

5. Conclusion

In each of the Figs. 1 to 3 the results for a fixed set of basis functions are given both for the original and the transformed Hamiltonian. For small coupling constants ($\lambda \leqq 0.5$) the results in the transformed picture are the better ones which one would expect, since the transformation yields an exact diagonalization in the small coupling limit. For the groundstate and a choice up to 20 basis functions the "transformed" diagonalization (TD) is better than the "original" one (OD) in the whole coupling region.

A characteristic feature of the comparison of both diagonalization procedures is displayed in Fig. 5, where the first excited state ("one-phonon-state") is considered. It is realized that for any given number of basis function the TD-results remain closer together and are enveloped by the 2 OD-curves. For the $A_{1,2}$-states the OD is better than the TD, whereas for the E-state the TD is almost (perhaps even strictly) exact.

Another remarkable result of the TS is exhibited in Figure 4. It is numerically found that the $E^{(1)}$-state over the whole coupling region practically does not depend on the number of basis functions within the fundamental set. One therefore could suspect that for this particular state the exponential transformation yields an exact eigenstate. But this suspicion has not been verified analytically.

For the Ham factors the comparison of both diagonalization procedures also yields an interesting characteristic property. It is generally found that in the OD the Ham-factors are approached from above and in the TD from below.

In conclusion it cannot be generally stated that in the strong coupling limit the TD procedure is more accurate than the OD, although this is true

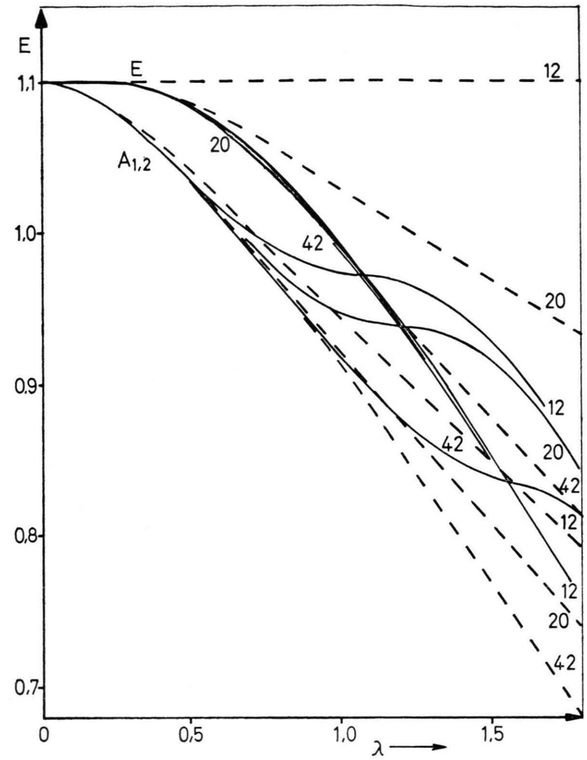

Fig. 5. One-phonon states of the E–e-problem. $\lambda = \varkappa/\omega$ is the coupling strength. Diagonalization in the original picture and after applying the exponential transformations given in the text. ----- original picture, ——— transformed picture. The numbers which are attached to the single curves denote the respective number of functions in the basic sequence.

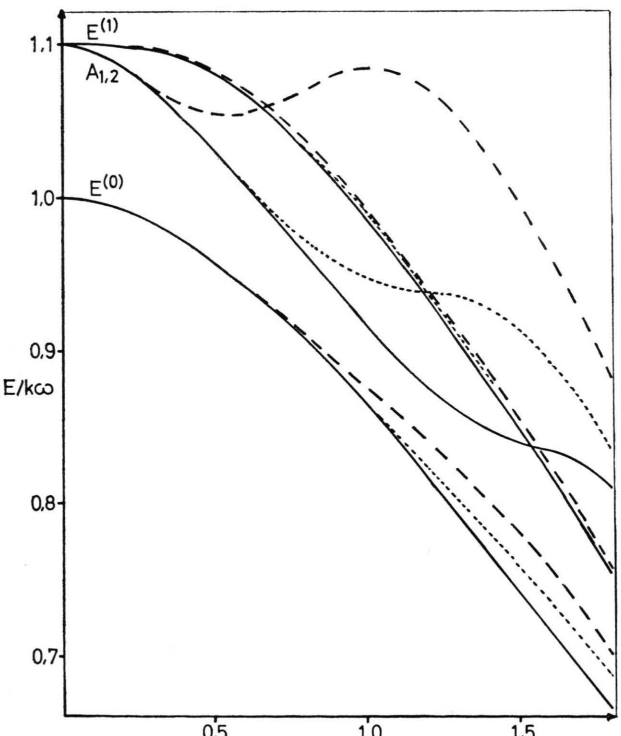

Fig. 4. Eigenvalues of the E–e-problem. $\lambda = \varkappa/\omega$ is the coupling strength. Diagonalization after performing an exponential transformation with an increasing extension of the basic sequence. ----- 6 basic functions, · · · · · 20 basis functions, ——— 42 basis functions.

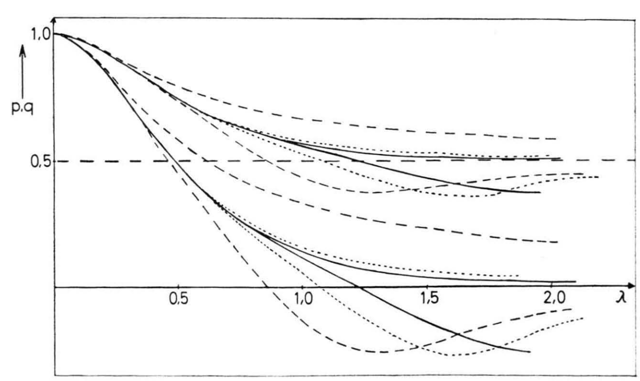

Fig. 6. Ham factors for the E–e-problem. $\lambda = \varkappa/\omega$ is the coupling strength. In the original picture the final result is approached from above, in the transformed picture from below. ----- 6 basis functions, · · · · · 20 basis functions, ——— 42 basis functions.

for specific states. However, the main value of the calculation in the transformed space lies in the fact that the exact result is approached in a different manner than within the conventional diagonalization procedure. Hence, both procedures can be used to cheque each other and to establish in this way a state of reliability which the conventional procedure does not have in view of the coupling of far-distant states. On the other hand, the comparison of numerical results as presented in this note and the numerical observation that in a calculation within the transformed frame some particular states are given with much higher accuracy than others, may serve as a guide to discuss and possibly improve the exponential transformation itself.

Appendix A:

Evaluation of the Matrix Elements $H^{ij}_{n_1, n_2, m_1, m_2}$

We first perform the integration over the electronic space,

$$\begin{aligned}\langle i; n_1, n_2 | \tilde{H} | j; m_1, m_2 \rangle = \delta_{i,j} \Big\{ & (\Omega - \omega \lambda^2 + \omega) \, \delta_{n_1, m_1} \cdot \delta_{n_2, m_2} \\ & - 2\omega \lambda^2 \sum_{n=0}^{\infty} \frac{(4\lambda^2)^n (2n+1)}{(2n+2)!} \langle n_1, n_2 | (\beta^2 + \gamma^2)^n | m_1, m_2 \rangle \\ & + 4\omega \lambda^3 (-1)^{i+1} \sum_{n=0}^{\infty} \frac{(4\lambda^2)^n (2n+2)}{(2n+3)!} \langle n_1, n_2 | (\beta^2 + \gamma^2)^n (\beta - 2\gamma (b_1^+ b_2 - b_2^+ b_1)) | m_1 m_2 \rangle \Big\} \\ & + (1 - \delta_{i,j}) \Big\{ (-1)^i 4\omega \lambda^2 \sum_{n=0}^{\infty} \frac{(4\lambda^2)^n (2n+1)}{(2n+2)!} \langle n_1, n_2 | (\beta^2 + \gamma^2)^n (b_1 b_2^+ - b_1^+ b_2) | m_1 m_2 \rangle \\ & + 4\omega \lambda^3 \sum_{n=0}^{\infty} \frac{(4\lambda^2)^n (2n+2)}{(2n+3)!} \langle n_1, n_2 | (\beta^2 + \gamma^2)^n (\gamma + 2\beta (b_1^+ b_2 - b_2^+ b_1)) | m_1, m_2 \rangle \Big\} . \end{aligned} \tag{A.1}$$

Applying the respective operators

$$\beta - 2\gamma (b_1^+ b_2 - b_2^+ b_1) , \quad b_1^+ b_2 - b_1^+ b_2 \quad \text{and} \quad \gamma + 2\beta (b_1^+ b_2 - b_2^+ b_1)$$

the remaining matrix elements in (A.1) may all be brought to the form

$$M = \langle n_1, n_2 | (\beta^2 + \gamma^2)^n | m_1, m_2 \rangle = \sum_{m=0}^{n} \binom{n}{m} \langle n_1 | \beta^{2n-2m} | m_1 \rangle \langle n_2 | \gamma^{2m} | m_2 \rangle . \tag{A.2}$$

The remaining integrals $\langle n_1 | \beta^{2n-2m} | m_1 \rangle$ and $\langle n_2 | \gamma^{2m} | m_2 \rangle$ do not disappear only if respectively n_1 and m_1 or n_2 and m_2 are either both even or both odd. Using this and

$$\begin{aligned}\langle n (b - b^+)^{2l} | n + 2\nu \rangle = \langle n + 2\nu | (b - b^+)^{2l} | n \rangle = \frac{\sqrt{(n+2\nu)!}}{n} \frac{(2l)!}{l!} (-1/2)^l (-2)^\nu \sum_{\varkappa=0}^{n} \frac{2^\varkappa}{(2\nu + \varkappa)!} \\ \cdot (l - \nu - \varkappa + 1)(l - \nu - \varkappa + 2) \cdots (l-1) \cdot l . \end{aligned} \tag{A.3}$$

and performing the summation over m for $n_2 = n_1 + 2\nu$, $m_2 = m_1 + 2\mu$ we get

$$\begin{aligned} M &= \langle n_1, n_2 | (\beta^2 + \gamma^2)^n | n_1 + 2\nu, n_2 + 2\mu \rangle \\ &= \sqrt{n_1+1} \sqrt{n_1+2} \cdots \sqrt{n_1 + 2\nu} \cdot \sqrt{n_2+1} \sqrt{n_2+2} \cdots \sqrt{n_2 + 2\mu} \cdot (-2)^n \cdot n! \, (-1)^{\nu+\mu} \\ & \cdot \sum_{\varkappa=0}^{n_1} \sum_{l=0}^{n_2} \binom{n}{\nu + \mu + \varkappa + l} \binom{n_1}{\varkappa} \binom{n_2}{l} \frac{(2\nu + 2\varkappa - 1)!! \, (2\mu + 2l - 1)!!}{(2\nu + \varkappa)! \, (2\mu + l)!} . \end{aligned} \tag{A.4}$$

[1] H. C. Longuet-Higgins, Proc. Roy. Soc. London **A 244**, 1 (1958).

[2] H. Uehara, J. Chem. Phys. **45**, 12 (1966).

[3] M. Wagner, Z. Physik **256**, 291 (1972).

[4] F. S. Ham, Phys. Rev. **B 166**, 307 (1968).

[5] E. Sigmund, M. Wagner, and M. Birkhold, Solid State Commun. **22**, 719 (1977).