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Coherent Motion of an Exciton in a Semi-Infinite Chain

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An explicit analytic expression for the propagator of a coherent motion of an exciton in a semi-infinite linear chain is derived. The "surface" relaxation is studied and the probability of an exciton being captured at the surface is calculated. The possibility of using the exponential decay approximation and the generalization to the three-dimensional crystal are also discussed.

1. Introduction

The propagation of quasiparticles like Frenkel exciton in a periodic lattice of a molecular crystal has been actively investigated [1] and the effect of the degree of the transport coherence on the motion has been recently studied in detail [2-4]. In this work the coherent transport limit as described by the time dependent Schrödinger equation (SE) is studied. The semi-infinite linear chain described by the effective hamiltonian with the nearest neighbour interaction is used, as the propagator can be found analytically in this simple case. Up to now, only the propagator for the infinite periodic chain has been published [2].

The role of the surface in the excitonic problem has been recently summarized in [5] within the limits of the stationary solutions of SE. In this work the surface is modeled in the standard way as the end site shift of the effective hamiltonian, but we are able to discuss not only the stationary states, but the full propagator that can again be calculated analytically. That makes possible to study in detail the effect of the surface shift upon the propagation of an excitation, namely to calculate the probability of an exciton being captured at the surface.

When one studies the decay of an excitation at the given site a question arises, if the standard exponential decay could be used to describe the effect. As we know the decay analytically in our system, we test the Golden Rule prediction and find it failing.

2. Stationary States in a Semi-Infinite Chain

We assume the motion of the exciton can be described by the effective hamiltonian

$$\hat{H}=\sum_{n=1}^{\infty}|n\rangle\alpha\langle n|+|n\rangle\beta\langle n+1|+|n+1\rangle\beta\langle n| + |1\rangle\Delta\alpha\langle 1| \tag{1}$$

where $|n\rangle$ is a state corresponding to the local excitation at the site $n=1, 2, 3, \ldots$, β is the nearest neighbour interaction and α is the diagonal matrix element of the hamiltonian. The relaxation at the surface is allowed for by changing the surface α to $\alpha+\Delta\alpha$. We assume the hamiltonian (1) describes the one-dimensional semi-infinite chain, but our results will be later changed to the three-dimensional case as well.

The spectrum of the hamiltonian (1) is well known [5, 6]. The eigenstates are searched for in the form

$$|\psi\rangle=\sum_{n=1}^{\infty}c_n|n\rangle \tag{2}$$

and the stationary SE takes the form of the infinite set of difference equations for the amplitudes c_n

$$-2X\,c_n+c_{n+1}+c_{n-1}=0, \quad X=(E-\alpha)/2\beta, \quad n=2, 3, \ldots \tag{3}$$

where E is the corresponding energy. The solution of (3) is

$$c_n = A_1 \cos(n\vartheta) + A_2 \sin(n\vartheta),\quad X = \cos\vartheta,\ \vartheta \in (0, \pi) \tag{4}$$

where constants A_1, A_2 must be chosen to satisfy the boundary condition at the surface

$$(-2X + q)\, c_1 + c_2 = 0, \qquad q = \Delta\alpha/\beta. \tag{5}$$

To satisfy (5) we set

$$A_1 = A(\vartheta)\, q \sin\vartheta, \qquad A_2 = A(\vartheta)(1 - q\cos\vartheta) \tag{6}$$

where $A(\vartheta)$ is the normalization factor found from the orthogonality relation $\langle\psi_\vartheta|\psi_{\vartheta'}\rangle = \delta(\vartheta - \vartheta')$ to be

$$A(\vartheta) = \sqrt{2/\pi}\,(1 - 2q\cos\vartheta + q^2)^{-1/2}. \tag{7}$$

From (4), (6), (7) we finally find the eigenstates (2) to be

$$|\psi_\vartheta\rangle = \sqrt{2/\pi}\,(1 - 2q\cos\vartheta + q^2)^{-1/2} \cdot \sum_{n=1}^{\infty} (\sin(n\vartheta) - q\sin(n-1)\vartheta)|n\rangle. \tag{8}$$

In addition to the bulk states a surface state appears above (below) the band $E = \alpha + 2\beta\cos\vartheta$ if $q > 1$ ($q < -1$). The energy of the surface state is [6]

$$E_b = \beta(q + q^{-1}) + \alpha \tag{9}$$

and the corresponding wave function

$$|\psi_b\rangle = (q^2 - 1)^{1/2} \sum_{n=1}^{\infty} q^{-n}|n\rangle, \qquad |q| > 1 \tag{10}$$

is getting damped with increasing n.

The inverse transformation to (8) and (10) is

$$|m\rangle = \sqrt{2/\pi}\int_0^\pi d\vartheta\, \frac{\sin(m\vartheta) - q\sin(m-1)\vartheta}{(1 - 2q\cos\vartheta + q^2)^{1/2}}\,|\psi_\vartheta\rangle + (q^2 - 1)^{1/2} q^{-m}|\psi_b\rangle \tag{11}$$

where the last term is missing, when $|q| < 1$.

3. The Exciton Propagator

The initial condition $|\Psi(0)\rangle$ must be specified before one attempts to construct a solution $|\Psi(t)\rangle$ of the time dependent SE. This is a rather involved problem, as the initial condition depends on the experimental set up and the properties of the sample studied (e.g. its absorption coefficient). Generally, however, any solution $|\Psi(t)\rangle$ can be found as a proper linear combination

$$|\Psi(t)\rangle = \sum_{m=1}^{\infty} b_m |\Psi_m(t)\rangle = \sum_{n=1}^{\infty} |n\rangle \sum_{m=1}^{\infty} b_m \langle n|\Psi_m(t)\rangle \tag{12}$$

where $|\Psi_m(t)\rangle$ is a solution of the time dependent SE satisfying the initial condition $|\Psi_m(0)\rangle = |m\rangle$ and $\Psi_{nm} = \langle n|\Psi_m(t)\rangle$ is the propagator or the probability amplitude of the excitation localized at $t = 0$ at the site m to be found at the site n at time t. Apart of its general importance (as it is displayed by (12)) the propagator $\Psi_{nm}(t)$ has a direct physical meaning as well: e.g. if the surface is coated with a monolayer of the different material (a surface shift $\Delta\alpha \neq 0$ in our model), it can be selectively excited by the radiation at time $t = 0$ and the propagator $\Psi_{n1}(t)$ describes the propagation of this excitation in time.

We find the propagator $\Psi_{nm}(t)$ as the time evolution of (11).

$$\begin{aligned}\Psi_{nm}(t) &= \langle n|\Psi_m(t)\rangle\\ &= (2/\pi)\int_0^\pi (1 - 2q\cos\vartheta + q^2)^{-1}\{\sin(m\vartheta) - q\sin((m-1)\vartheta)\}\\ &\quad\cdot[\sin(n\vartheta) - q\sin((n-1)\vartheta)]\, e^{-2it\cos\vartheta} d\vartheta\\ &\quad + (q^2 - 1)\, q^{-(n+m)} e^{-it(q+q^{-1})}\end{aligned} \tag{13}$$

(time is measured in the units $\beta/\hbar$ throughout this paper). Cases $|q| < 1$, $|q| > 1$ and $q = 1$ will now be treated separately.

For $|q| < 1$ we expand the square of the normalization coefficient (7) into the Chebyshev polynomials (A 5) and using simple trigonometric formulae we transform (13) into the form (there is no surface state contribution in (13) for $|q| < 1$)

$$\begin{aligned}\langle n|\Psi_m(t)\rangle &= (2/\pi)\int_0^\pi \sin(n\vartheta)\sin(m\vartheta)\, e^{-2it\cos\vartheta} d\vartheta\\ &\quad + (2/\pi)\sum_{j=1}^{\infty} q^j \int_0^\pi \sin(\vartheta)\sin(j + m + n - 1)\vartheta\, e^{-2it\cos\vartheta} d\vartheta.\end{aligned} \tag{14}$$

Rewriting the product of sines as a cosine difference, one can evaluate integrals in terms of the Bessel functions (see (A 1–A 3)):

$$\langle n|\Psi_m(t)\rangle = (-i)^{n-m}[J_{n-m}(2t) - (-1)^m J_{n-m}(2t)] + \sum_{j=1}^{\infty} q^j(-i)^{m+j+n}(m + j + n - 1)\, J_{m+j+n-1}(2t)/t. \tag{15}$$

The expansion (15) has a simple meaning: it is just the Born series for the propagator $\Psi_{nm}(t)$

$$\hat{G} = \hat{G}^0 + \hat{G}^0\,\hat{\Delta}\,V\hat{G}^0 + \hat{G}^0\,\hat{\Delta}\,V\hat{G}^0\,\hat{\Delta}\,V\hat{G}^0 + \ldots$$

where $\hat{G}^0$ is the propagator for the unperturbed simi-infinite chain as given by the first term in (15) and $\hat{\Delta} V$ is the perturbative potential $\Delta V = |1\rangle q \langle 1|$.

When $|q|>1$ the surface state is present. The scattering is strong and the Born series does not converge. Introducing a small parameter $s=1/q$ and expanding the normalization factor in powers of s, one gets in a similar way as before

$$\langle n|\Psi_m(t)\rangle = (2/\pi)\int_0^\pi \mathrm{d}\vartheta \sin(n-1)\vartheta \sin(m-1)\vartheta\, \mathrm{e}^{-2it\cos\vartheta}$$
$$+\sum_{j=1}^{\infty} s^j (2/\pi)\int_0^\pi \mathrm{d}\vartheta \sin\vartheta \sin(m+n-j-1)\vartheta\, \mathrm{e}^{-2it\cos\vartheta}$$
$$+(1-s^2)\, s^{m+n-2}\, \mathrm{e}^{-it(s+s^{-1})}, \quad |s|<1. \tag{16}$$

The first term describes again propagation in a perfect semi-infinite chain that is now, however, decoupled from the first site ($\Delta\alpha \to \infty$ limit). The second term gives the rest of the continuum contribution to the propagation, while the third one is a surface state part. The integrals in (16) can again be expressed in terms of the Bessel functions

$$\langle n|\Psi_m(t)\rangle = (-i)^{n-m}[J_{n-m}(2t)+(-1)^m J_{n+m-2}(2t)]$$
$$+\sum_{j=1}^{\infty} s^j(-i)^{m+n-j}(m+n-j-1)\, J_{m+n-j-1}(2t)/t$$
$$+(1-s^2)\, s^{m+n-2}\, \mathrm{e}^{-it(s+s^{-1})}, \quad s=1/q, \quad |s|<1. \tag{17}$$

Finally, for $q=1$ the expression (15) can be summed or, alternatively, Eq. (13) can be evaluated directly. Both results coincide giving

$$\langle n|\Psi_m(t)\rangle$$
$$=(-i)^{n+m-1}[J_{n+m-1}(2t)-i(-1)^m J_{n-m}(2t)]. \tag{18}$$

4. The Exciton Propagation

We shall illustrate the time propagation of an exciton created at time $t=0$ at the site m by plotting the probability $P_{nm}(t)=|\langle n|\Psi_m(t)\rangle|^2$, $n=1, 2, 3, 4$ and 5 that at time t the exciton is found at the site n.

The propagation following the excitation at the surface site ($m=1$) is illustrated in Figs. 1 and 2. In Fig. 1 the probabilities describe the situation when there is no surface relaxation ($q=0$, full line) and when the surface state is just to appear ($q=1$, dashed line). The exciton can be seen to propagate from the "surface" into the "bulk" and in the same time it spreads out. With increasing q, the rate of a decay at the given site is slowing down.

The presence of a surface state changes the situation dramatically, as shown in Fig. 2 (full line) for $q=2$ ($E_b=2.5\beta$). Note that the probability does not decay in the surface region and, consequently, there is a large chance that the exciton has been captured at the surface. Once the exciton manages to leave the "region of the surface state", it propagates and spreads out as in Fig. 1.

Exciting at $t=0$ the third site ($m=3$) rather then the surface site ($m=1$), the probability shows the characteristic double peak structure that is best displayed in Fig. 3 (full line) for $q=0$. It results from the superposition of two probability waves: a wave propagat-

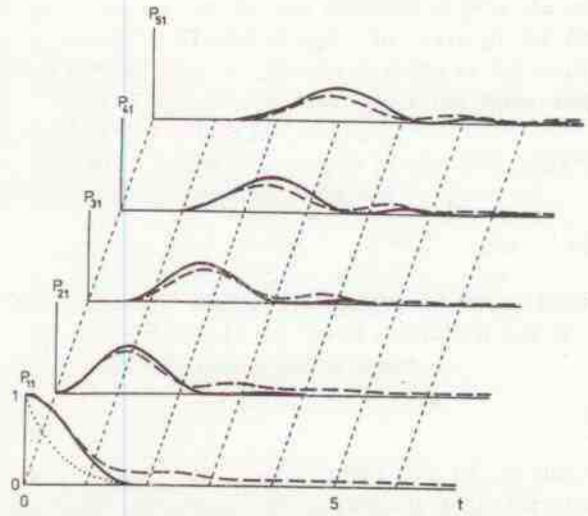

Fig. 1. The probability propagator $P_{n1}(t)=|\langle n|\Psi_1(t)\rangle|^2$ (surface excitation) for $n=1, \ldots, 5$ as calculated from (15). The surface perturbation $q=\Delta\alpha/\beta$ shown are $q=0$ (full line) and $q=1$ (dashed line). The $P_{11}(t)$ as calculated from exponential decay (see (25, 29)) is shown as dotted line. Time in all figures is measured in $\hbar/\beta$ units

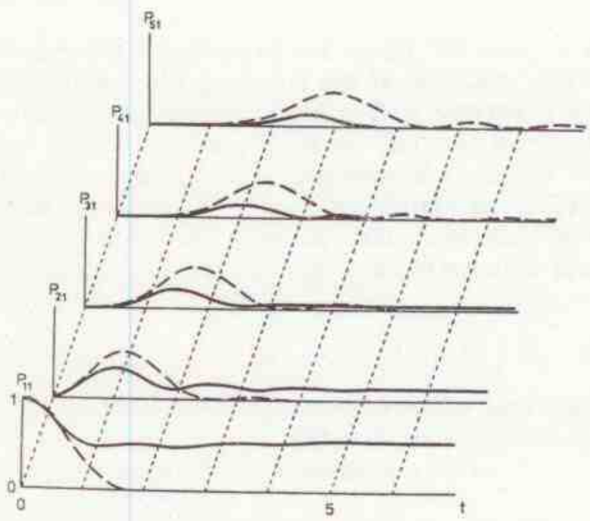

Fig. 2. The probability propagator $P_{n1}(t)$, for $n=1, \ldots, 5$ as calculated from (17) for $q=2$ (full line). For comparison the full curve from Fig. 1 ($P_{n1}(t)$ for $q=0$) is also shown as dashed curve

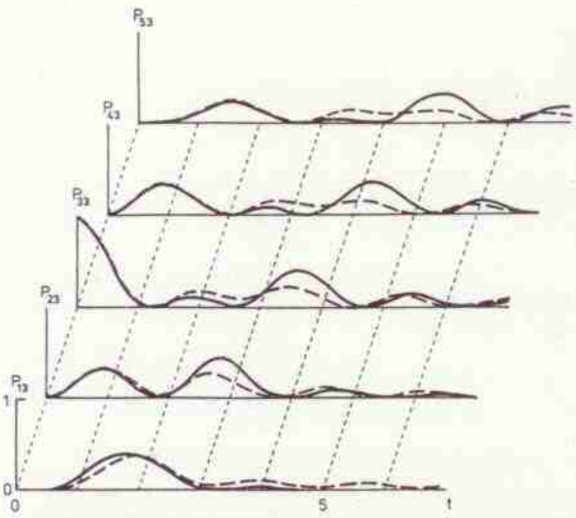

Fig. 3. The probability propagator $P_{n3}(t)$ for $n=1, \ldots, 5$ as calculated from (15) for $q=0$ (full line) and from (18) for $q=1$ (dashed line)

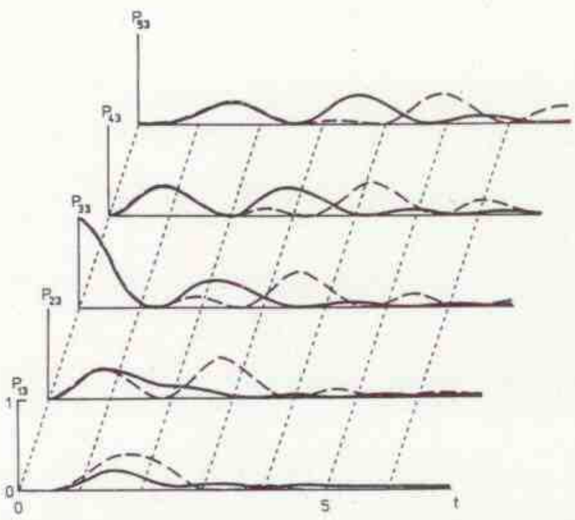

Fig. 4. The probability propagator $P_{n3}(t)$ for $n=1, \ldots, 5$ as calculated from (17) for $q=2$ (full line). For comparison the full curve from Fig. 3 ($P_{n3}(t)$ for $q=0$) is also shown as dashed line

ing directly from the excitation site and a wave reflected from the end of a chain. When the surface state is just to appear as in Fig. 3 (broken line, $q=1$), the exciton is delayed at the surface and the reflected wave becomes rather broad at all sites. When the surface state does exist (see Fig. 4, full line) the reflected structure, surprisingly, becomes rather sharp again and more like the simple propagation in Fig. 3 (full line). On the other hand there is again a small chance of the exciton being captured forever at the surface. What happens is that with growing q the first site becomes effectively decoupled from the rest of a chain and the second site becomes to play the role of a surface: correspondingly, the wave at the first site is diminishing and the wave shape at the second site in Fig. 4 (full line) is much alike the wave shape at the first site in Fig. 3.

The probability the exciton is actually captured can be calculated exactly from (17)

$$P_{nm}(\infty)=\{(1-s^2)\, s^{m+n-2}\}^2, \quad s=1/q, \quad |s|<1. \quad (19)$$

The maximum chance the exciton is found bound at the surface ($n=1$) for given excitation site m, is achieved for the surface perturbation

$$q=[(m+1)/(m-1)]^{1/2}. \quad (20)$$

From (20) one gets $q \to \infty$ in the case of the surface excitation and from (19) $P_{11}(\infty)=1$, while for $m=3$ the maximum effect corresponds to $q=\sqrt{2}$ and, correspondingly, $P_{13}(\infty)=0.06$.

5. The Golden Rule

Due to the simplicity of our model, the decay of the excitation at the given site can be calculated exactly; usually, however, the Golden Rule formula is used for these problems. To show that our probability $P_{11}(t)$ corresponds to a problem of a discrete level decaying into a continuum, we reformulate our problem as follows: assuming the surface excitation ($m=1$) we split the state $|1\rangle$ from the rest and write the hamiltonian (1) accordingly as

$$\hat{H}=|1\rangle(\alpha+\Delta\alpha)\langle 1|+\{|1\rangle\, \beta\langle 2|+|2\rangle\, \beta\langle 1|\}+\hat{H}'. \quad (21)$$

The last term $\hat{H}'$ is the hamiltonian of a semi-infinite lattice with the first site removed. Its eigenstates $|\varphi_\vartheta\rangle$ are given by (8) with the change $n \to n-1$

$$|\varphi_\vartheta\rangle=\sqrt{2/\pi}(1-2\cos\vartheta+q^2)^{-1/2} \cdot \sum_{n=2}^{\infty}[\sin(n-1)\vartheta-q\sin(n-2)\vartheta]\,|n\rangle. \quad (22)$$

In the basis $\{|1\rangle, |\varphi_\vartheta\rangle\}$ the hamiltonian $\hat{H}'$ is diagonal

$$\hat{H}'=\int_0^\pi \{|\varphi_\vartheta\rangle\{\alpha+2\beta\cos\vartheta\}\langle\varphi_\vartheta|\}\, d\vartheta \quad (23)$$

and the middle term in (21) is the interaction hamiltonian

$$\hat{H}_{\text{int}}=\beta\sqrt{2/\pi}\int_0^\pi d\vartheta(1-2\cos\vartheta+q^2)^{-1/2} \cdot \sin\vartheta\{|1\rangle\langle\varphi_\vartheta|+|\varphi_\vartheta\rangle\langle 1|\} \quad (24)$$

coupling the level $E=\alpha+\Delta\alpha$ with the continuous band of states (23). When the excitation at the site $m=1$ is created at $t=0$, it decays into the continuum $|\varphi_\vartheta\rangle$ as a result of the coupling (24). If the Wigner-Weisskopf (WW) theory [7] is now assumed to be plausible, the lifetime of the initial state T is introduced

$$\langle 1|\Psi_1(t)\rangle=\exp(-t/2T) \tag{25}$$

in accordance with an assumed exponential decay of the initial state and the lifetime is calculated from the standard expression

$$1/T=2\pi/\hbar\{|\langle 1|\hat{H}_{\text{int}}|\varphi_\vartheta\rangle|^2 g(E)\}_{E(\vartheta)=\alpha+\Delta\alpha} \tag{26}$$

where $g(E)$ is the density of states in the band.

The formula (26) can be evaluated analytically. For the transition matrix element we get from (23)

$$\langle 1|\hat{H}_{\text{int}}|\varphi_\vartheta\rangle=\beta\sqrt{2/\pi}\,\sin\vartheta/(1-2q\sin\vartheta+q^2)^{1/2} \tag{27}$$

and the density of states is

$$g(E)=\frac{\mathrm{d}\vartheta}{\mathrm{d}E}=1/[4\beta^2-(\alpha-E)^2]^{1/2}. \tag{28}$$

Using (27) and (28) in (26) we find

$$1/T=2(1-q^2/4)^{1/2}\beta/\hbar, \quad |q|<1. \tag{29}$$

The exponential decay (25), (29) is compared with the exact result in Fig. 1 (dotted line) and it turns out to be rather poor approximation. The reason can be traced to the failure of various approximations inherent to the use of WW theory (e.g. the width of the excited state $\Delta E=\hbar/T$ should be much smaller then the band width 4β).

6. Generalization to the Three-Dimensional Crystal

Let us consider a cubic crystal with (100) surface described by the nearest neighbour hamiltonian analogous to (1). We shall label the lattice sites (i, j, k) and assume, for the sake of simplicity, that the diagonal matrix element of the hamiltonian, α, is zero, except for the $i=1$ surface layer, where it is equal $\Delta\alpha$. The corresponding time dependent SE for the amplitudes $c_{i,j,k}=\langle i,j,k|\Psi(t)\rangle$ is

$$i\hbar\frac{\mathrm{d}c_{i,j,k}}{\mathrm{d}t}=\Delta\alpha\,\delta_{i,1}\,c_{i,j,k}+\beta[(1-\delta_{i,1})\,c_{i-1,j,k}+c_{i+1,j,k}+c_{i,j-1,k}+c_{i,j+1,k}+c_{i,j,k-1}+c_{i,j,k+1}] \tag{30}$$

where $i=1, 2, \ldots; j, k=\ldots -2, -1, 0, 1, 2, \ldots$ and the factor $(1-\delta_{i,1})$ takes into account that there is no $i=0$ layer. The separation of variables $c_{i,j,k}=u_i v_j w_k$ transforms (30) into three one-dimensional problems. The first one, for u_i amplitudes

$$i\hbar\frac{\mathrm{d}u_i}{\mathrm{d}t}=\Delta\alpha\,\delta_{i,1}\,u_i+\beta[(1-\delta_{i,1})\,u_{i-1}+u_{i+1}] \tag{31}$$

is identical to the problem of a semi-infinite chain solved in this work (apart for the choice $\alpha=0$). The equations for v_m and w_n amplitudes describes the motion of an exciton in an infinite chain along the j and k directions. Since the corresponding propagators are known, we conclude that the exciton propagator for our three-dimensional semi-infinite crystal can be written as the product of the corresponding three one-dimensional propagators

$$\Psi_{ijk;i'j'k'}(t)=\Psi_{ii'}(t)[(-i)^{j-j'}J_{j-j'}(2t)][(-i)^{k-k'}J_{k-k'}(2t)]$$

where $\Psi_{ii'}(t)$ is the propagator given by (15), (17) and (18) and $(-i)^m J_m(2t)$ is the propagator for the infinite chain (see [2]).

This work was stimulated by the collaboration with professor V.M. Kenkre from the University of New Mexico, where one of the authors (L.S.) had the pleasure to work.

Appendix

The notation and definition of the Bessel functions used here are those of Abramowitz and Stegun [8]. We list below some formulas used repeatedly here (they can all be found in [8]).

$$\pi^{-1}\int_0^\pi \cos(n\vartheta)\,e^{-iz\cos\vartheta}\,\mathrm{d}\vartheta=(-i)^n J_n(z), \tag{A1}$$

$$J_n(-z)=(-1)^n J_n(z), \tag{A2}$$

$$J_n(z)=(-1)^n J_{-n}(z), \tag{A3}$$

$$J_{n-1}(z)+J_{n+1}(z)=2nJ_n(z)/z. \tag{A4}$$

The expansion of the squared normalization factor (7) into the Chebyshev polynomials is

$$(1-2q\cos\vartheta+q^2)^{-1}=\sum_{m=0}^{\infty}(\sin(m+1)\vartheta/\sin\vartheta)\,q^m, \quad 0<q<1. \tag{A5}$$

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