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Exact and phase-integral quantal matrix elements of a function, corresponding to a damped oscillation, between unbound states for a particle in a potential proportional to e^{-ax}

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Abstract. The Jackson-Mott formula, which gives an exact expression for the matrix elements of $\exp(-ax)$, where $a>0$, between unbound states for a particle moving in a real potential proportional to $\exp(-ax)$, has been generalised by Mies for states with different potentials (but with the same a). Eno and Balint-Kurti generalised the formula further to matrix elements of $\exp(-ax)$ raised to an arbitrary positive power. In the present treatment we make a further generalisation to matrix elements of a function corresponding to a damped oscillation $\exp(-\gamma ax)$, where γ is a complex number, between unbound states for a particle moving in a potential proportional to $\exp(-ax)$, where $a>0$. For the diagonal and non-diagonal matrix elements the resulting exact formula is compared to the corresponding phase-integral formula. When certain conditions are fulfilled, the respective phase-integral formula gives a very satisfactory result.

1. Introduction

In a paper concerning the energy exchange between inert gas atoms Jackson and Mott (1932) gave an exact expression for the quantal matrix elements $\langle k, c|\exp(-ax)|k', c\rangle$ of $\exp(-ax)$, where $a>0$, between unbound states for a particle in the potential $\exp(-ax)a^2c^2\hbar^2/2m$, where c is a real dimensionless parameter. Mies (1964) generalised the Jackson-Mott formula for $\langle k, c|\exp(-ax)|k', c\rangle$ into a formula for $\langle k, c|\exp(-ax)|k', c'\rangle$. Eno and Balint-Kurti (1977) generalised the formula further into a formula for the matrix elements of $\exp(-ax)$ raised to an arbitrary positive power, and applied it to the calculation of inelastic molecular collision cross sections. In the present work we make a further generalisation and obtain formulae for $\langle k, c|\exp(-\gamma ax)|k', c'\rangle$, where $\mathrm{Re}\,\gamma>0$, $\mathrm{Re}\,c>0$, $\mathrm{Re}\,c'>0$. The reason for making such a generalisation is that we want to study matrix elements of a possibly oscillating function, and sufficiently general formulae for exactly soluble models do not seem to be available in the literature, as far as unbound states are concerned. There is another good candidate (apart from the model problem treated in the present paper), namely the exact bound-state matrix element obtained by Myhrman (1983), which should be possible to generalise to unbound states and an oscillating function. It goes without saying that a model problem, for which the matrix elements between unbound states of a function corresponding to a damped oscillation can be obtained in a rather simple closed form, should have a wide range of applicability.

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Fröman *et al* (1985) have recently used the Jackson–Mott formula for investigating the accuracy of a phase-integral formula for the matrix elements involving unbound states (Fröman *et al* 1979); the phase-integral formula was found to be very satisfactory. In the present paper we demonstrate that the phase-integral diagonal and non-diagonal matrix elements of a function corresponding to a smooth or rather smooth damped oscillation are also very accurate for one-turning-point problems. For a function which oscillates too strongly, however, the accuracy becomes rather mediocre or even poor. This is in agreement with bound-state matrix element results, reported by Fröman and Fröman (1977).

2. The model Schrödinger equation and its acceptable solution

The one-dimensional Schrödinger equation for a particle with the energy $\hbar^2k^2/2m>0$ moving in the potential $\exp(-ax)a^2c^2\hbar^2/2m$ can be written

$$d^2u/dx^2+R(x)u=0 \qquad -\infty<x<\infty \tag{1a}$$

where

$$R(x)=R_{k,c}(x)=k^2-a^2c^2\exp(-ax). \tag{1b}$$

We shall assume a to be real and positive:

$$a>0 \tag{2a}$$

and c to be complex with a positive real part:

$$\mathrm{Re}\ c>0. \tag{2b}$$

Thus we exclude the case of real negative values of c^2.

The particular solution $u_{k,c}(x)$ of (1a, b), which tends to zero as $x\to-\infty$ and tends to a sine function with the prefactor unity as $x\to+\infty$, is

$$u_{k,c}(x)=[2k/(\pi a)\sinh(2\pi k/a)]^{1/2}K_{2ik/a}(2c\exp(-\tfrac{1}{2}ax)) \qquad \mathrm{Re}\ c>0 \tag{3}$$

where $K_\nu(cz)$ is the modified Bessel function of the third kind. In fact, according to equation (9.6.24) in Abramowitz and Stegun (1965) this solution can be rewritten as

$$\begin{aligned}u_{k,c}(x)&=[k/(2\pi a)\sinh(2\pi k/a)]^{1/2}\int_{-\infty}^{+\infty}\exp[-2c\exp(-\tfrac{1}{2}ax)\cosh y]\cos(2ky/a)\,dy\\&=(2\pi k/a)^{-1/2}[\sinh(2\pi k/a)]^{1/2}c\exp(-\tfrac{1}{2}ax)\\&\quad\times\int_{-\infty}^{+\infty}\exp[-2c\exp(-\tfrac{1}{2}ax)\cosh y]\sin(2ky/a)\,e^y\,dy \qquad \mathrm{Re}\ c>0\end{aligned} \tag{4}$$

where it is immediately seen that the second member tends to zero as $x\to-\infty$, and where the last member is obtained through integration by parts. Introducing into (4) the substitution

$$e^y=Y \tag{5}$$

we obtain with the aid of equations (6.1.31) and (6.1.1) in Abramowitz and Stegun (1965)

$$\begin{aligned} u_{k,c}(x) &= |\Gamma(1+2ik/a)|^{-1}\frac{c\exp(-\frac{1}{2}ax)}{2i}\int_0^\infty \exp[-c\exp(-\tfrac{1}{2}ax)(Y+Y^{-1})] \\ &\quad\times(Y^{2ik/a}-Y^{-2ik/a})\,dY \\ &= |\Gamma(1+2ik/a)|^{-1}\Bigg(\frac{c\exp(-\frac{1}{2}ax)}{2i}\int_0^\infty \exp[-cY\exp(-\tfrac{1}{2}ax)] \\ &\quad\times(Y^{2ik/a}-Y^{-2ik/a})\,dY \\ &\quad-\frac{c\exp(-\frac{1}{2}ax)}{2i}\int_0^\infty \{1-\exp[-cY^{-1}\exp(-\tfrac{1}{2}ax)]\} \\ &\quad\times\exp[-cY\exp(-\tfrac{1}{2}ax)](Y^{2ik/a}-Y^{-2ik/a})\,dY\Bigg) \\ &= \sin[kx-(k/a)\ln c^2+\arg\Gamma(1+2ik/a)] \\ &\quad+\frac{\frac{1}{2}ic\exp(-\frac{1}{2}ax)}{|\Gamma(1+2ik/a)|}\int_0^\infty \{1-\exp[-cY^{-1}\exp(-\tfrac{1}{2}ax)]\} \\ &\quad\times\exp[-cY\exp(-\tfrac{1}{2}ax)](Y^{2ik/a}-Y^{-2ik/a})\,dY \qquad \operatorname{Re} c>0. \end{aligned} \tag{6}$$

The second term on the right-hand side of (6) tends to zero as $x\to+\infty$, and hence

$$u_{k,c}(x)\sim\sin[kx-(k/a)\ln c^2+\arg\Gamma(1+2ik/a)] \qquad x\to+\infty \qquad \operatorname{Re} c>0. \tag{7}$$

3. Calculation of the exact matrix element

We shall now calculate the matrix element

$$\langle k,c|\exp(-\gamma ax)|k',c'\rangle=\int_{-\infty}^{+\infty}u_{k,c}(x)\exp(-\gamma ax)u_{k',c'}(x)\,dx$$

$$\operatorname{Re} c>0 \qquad \operatorname{Re} c'>0 \tag{8}$$

where $u_{k,c}(x)$ is the acceptable solution given by (3), and where

$$\operatorname{Re}\gamma>0 \tag{9}$$

in order that the integral on the right-hand side of (8) be convergent.

Substituting (3) into (8) and making in the resulting formula the substitution

$$z=2\exp(-\tfrac{1}{2}ax) \tag{10}$$

we obtain

$$\begin{aligned} \langle k,c|\exp(-\gamma ax)|k',c'\rangle &= \frac{2^{1-2\gamma}}{\pi^2 a}[(2\pi k/a)\sinh(2\pi k/a)(2\pi k'/a)\sinh(2\pi k'/a)]^{1/2} \\ &\quad\times\int_0^\infty z^{2\gamma-1}K_{2ik/a}(cz)K_{2ik'/a}(c'z)\,dz \qquad \operatorname{Re} c>0 \\ &\quad \operatorname{Re} c'>0 \qquad \operatorname{Re}\gamma>0. \end{aligned} \tag{11}$$

Using equation (6.576:4) on p 693 in Gradshteyn and Ryshik (1980) or equation (49) on p 145 in Erdélyi (1953) together with equation (15.3.3) in Abramowitz and Stegun (1965), we obtain from (11) the following expression for the matrix element:

$$\begin{aligned}\langle k, c|\exp(-\gamma a x)|k', c'\rangle &= (4\pi^2 a)^{-1}[(2\pi k/a)\sinh(2\pi k/a)(2\pi k'/a)\sinh(2\pi k'/a)]^{1/2} c^{-2\gamma} \\ &\times \Gamma(\gamma + \mathrm{i}(k'+k)/a)\Gamma(\gamma + \mathrm{i}(k'-k)/a)\Gamma(\gamma - \mathrm{i}(k'+k)/a) \\ &\times \Gamma(\gamma - \mathrm{i}(k'-k)/a)\exp[\mathrm{i}(k'/a)\ln(c'^2/c^2)] \\ &\times {}_2F_1(\gamma + \mathrm{i}(k'+k)/a, \gamma + \mathrm{i}(k'-k)/a; 2\gamma; 1 - c'^2/c^2)/\Gamma(2\gamma) \qquad (12)\end{aligned}$$

which is valid under the assumptions $(2a, b)$ and (9). Alternatively, with the aid of equation (6.1.31) in Abramowitz and Stegun (1965) our final formula (12) can be rewritten as

$$\begin{aligned}\langle k, c|\exp(-\gamma a x)|k', c'\rangle &= (kk'/a^3)[\Gamma(1+2\mathrm{i}k/a)\Gamma(1-2\mathrm{i}k/a)\Gamma(1+2\mathrm{i}k'/a)\Gamma(1-2\mathrm{i}k'/a)]^{-1/2} \\ &\times c^{-2\gamma}\Gamma(\gamma + \mathrm{i}(k'+k)/a)\Gamma(\gamma + \mathrm{i}(k'-k)/a)\Gamma(\gamma - \mathrm{i}(k'+k)/a) \\ &\times \Gamma(\gamma - \mathrm{i}(k'-k)/a)\exp[\mathrm{i}(k'/a)\ln(c'^2/c^2)] \\ &\times {}_2F_1(\gamma + \mathrm{i}(k'+k)/a, \gamma + \mathrm{i}(k'-k)/a; 2\gamma; 1 - c'^2/c^2)/\Gamma(2\gamma). \qquad (12')\end{aligned}$$

If c' and c are real and if $\gamma = \alpha + \mathrm{i}\beta$, where $\alpha > 0$ and β is real, we obtain the matrix element $\langle k, c|\exp(-\alpha a x)\cos(\beta a x)|k', c'\rangle$ by taking the real part of the right-hand side of (12) or (12′) and $\langle k, c|\exp(-\alpha a x)\sin(\beta a x)|k', c'\rangle$ by taking the imaginary part of the same side.

For real values of γ, c' and c we obtain from (12) the generalised Mies formula (Eno and Balint-Kurti 1977). Putting $\gamma = 1$ and assuming c' and c to be real, we obtain the formula given by Mies (1964). Putting $\gamma = 1$ and $c' = c$ (real), we obtain the Jackson-Mott (1932) formula.

Formula (12) (or (12′)) is written in a form which is suitable for the evaluation of the matrix element when c' is equal to or close to c. When the ratio c'/c deviates strongly from unity one should at first use the linear transformation formulae for the hypergeometric function in (12) or (12′) (cf, e.g., chapter 15 in Abramowitz and Stegun (1965)) before making any analytical or numerical evaluations.

4. Comparison with the corresponding phase-integral formula for diagonal matrix elements

For the background of this section see appendix 1. In appendix 1 the choice of base function $Q(x)$ has been kept open, depending on the problem considered. In the present application we shall choose

$$Q(x) = R^{1/2}(x) \qquad (13)$$

where $R(x)$ is given by $(1b)$ and where for a real potential $Q(x)$ is positive on the upper lip of the cut emerging from the zero x_0 of Q^2 to the right along the real x axis.

Adapting and applying equation (A1.15) of appendix 1 to the exactly soluble model described previously in the present paper, we obtain with the aid of equation (13.2(6)) in Erdélyi (1953) and equation (6.1.8) and (6.1.18) in Abramowitz and Stegun (1965) for the phase-integral approximation of order $2N+1$

$$\langle k, c|\exp(-\gamma a x)|k, c\rangle_{\text{phase-integral}}$$

$$= \frac{1}{a}\frac{k^2/a^2}{c^{2\gamma}}\frac{[\Gamma(\gamma)]^2}{\Gamma(2\gamma)}(2k/a)^{2\gamma-2}\sum_{n=0}^{2N}\sum_{m=0}^{2N-n} \times \frac{(1-\gamma)_n(1-\gamma)_m}{n!\quad m!}\frac{B_n^{(\gamma)}B_m^{(\gamma)}}{(2ik/a)^n(-2ik/a)^m}$$

$$= \frac{1}{a}\frac{k^2/a^2}{c^{2\gamma}}\frac{[\Gamma(\gamma)]^2}{\Gamma(2\gamma)}(2k/a)^{2\gamma-2}\Bigg(\underset{(1)}{1} + \underset{(3)}{\frac{a^2}{24k^2}\gamma(\gamma-1)(2\gamma-1)} + \underset{(5)}{\frac{a^4}{5760k^4}\gamma(\gamma-1)(\gamma-2)(2\gamma-1)(2\gamma-3)(5\gamma+1)} + \ldots\Bigg)$$

$$\operatorname{Re} c > 0 \qquad \operatorname{Re}\gamma > 0 \tag{14}$$

where

$$(1-\gamma)_0 = 1 \tag{15a}$$

$$(1-\gamma)_n = (1-\gamma)(2-\gamma)\ldots(n-\gamma) \tag{15b}$$

and

$$B_n^{(\gamma)} = \frac{\mathrm{d}^n}{\mathrm{d}t^n}\left[\left(\frac{t}{\mathrm{e}^t-1}\right)^\gamma\right]_{t=0}. \tag{16}$$

In (14) the numbers in parentheses below the terms indicate the contributions from successive orders of the approximation. The explicit expressions for the first $B_n^{(\gamma)}$ are

$$B_0^{(\gamma)} = 1 \tag{17a}$$

$$B_1^{(\gamma)} = -\gamma/2 \tag{17b}$$

$$B_2^{(\gamma)} = \gamma(3\gamma-1)/12 \tag{17c}$$

$$B_3^{(\gamma)} = -\gamma^2(\gamma-1)/8 \tag{17d}$$

$$B_4^{(\gamma)} = \gamma(15\gamma^3-30\gamma^2+5\gamma+2)/240 \tag{17e}$$

$$B_5^{(\gamma)} = -\gamma^2(3\gamma^3-10\gamma^2+5\gamma+2)/96 \tag{17f}$$

$$B_6^{(\gamma)} = \gamma(63\gamma^5-315\gamma^4+315\gamma^3+91\gamma^2-42\gamma-16)/4032 \tag{17g}$$

$$B_7^{(\gamma)} = -\gamma^2(9\gamma^5-63\gamma^4+105\gamma^3+7\gamma^2-42\gamma-16)/1152 \tag{17h}$$

$$B_8^{(\gamma)} = \gamma(135\gamma^7-1260\gamma^6+3150\gamma^5-840\gamma^4-2345\gamma^3-540\gamma^2+404\gamma+144)/34\,560. \tag{17i}$$

Formula (14) has been obtained analytically for positive integral values of N up to 2, i.e. up to the terms given explicitly on the right-hand side of (14). For higher

values of N and certain numerical values of the parameters we have integrated numerically the right-hand side of (A1.15) in appendix 1, adapted and applied to the present problem, and found an agreement with the second member of (14) within the accuracy obtainable numerically.

Formula (14) is, for any order of approximation, expected to be rather mediocre as compared to the exact result in the previous section, if k/a is sufficiently small. This is due to the fact that (A1.15) in appendix 1 is a one-transition-point formula, and for the exponential potential there are other transition points in the complex plane, the contributions of which become important for sufficiently small values of k/a. Hence, the model potential in question can be used for testing (A1.15) in appendix 1 only when $2k/a \geqslant 1$.

Introducing the notation

$$P(\gamma;\ k/a) = \frac{\langle k,\ c|\exp(-\gamma a x)|k,\ c\rangle_{\text{phase-integral}}}{\langle k,\ c|\exp(-\gamma a x)|k,\ c\rangle} \tag{18}$$

we obtain from (14) and (13) with $k' = k$ and $c' = c$

$$P(\gamma;\ k/a) = \frac{\Gamma(1+2ik/a)\Gamma(1-2ik/a)}{\Gamma(\gamma+2ik/a)\Gamma(\gamma-2ik/a)}(2k/a)^{2\gamma-2} \times \sum_{n=0}^{2N}\sum_{m=0}^{2N-m}\frac{(1-\gamma)_n(1-\gamma)_m}{n!m!}\frac{B_n^{(\gamma)}B_m^{(\gamma)}}{(2ik/a)^n(-2ik/a)^m} \qquad \text{Re}\ \gamma > 0. \tag{19}$$

It should be noted that $P(\gamma;\ k/a)$ is independent of c; cf the comments following equation (31).

Putting $\gamma = r+\frac{1}{2}$, where r is a non-negative integer, we obtain from (19), with (15) and (16), with the aid of equations (6.1.15) and (6.1.30) in Abramowitz and Stegun (1965),

$$P(r+\tfrac{1}{2};\ k/a) = [1+\exp(-4\pi k/a)]/[1-\exp(-4\pi k/a)]$$
$$r = 0, 1, 2, \ldots;\ N \geqslant r \tag{20}$$

which means that for positive half-integral values of γ the phase-integral formula (14) is very accurate if $2k/a > 1$ and $N \geqslant \gamma - \frac{1}{2}$.

Putting instead $\gamma = r+1$ in (19) with (15) and (16), and using the recurrence formula (6.1.15) in Abramowitz and Stegun (1965), we obtain

$$P(r+1;\ k/a) = 1 \qquad r = 0, 1, 2, \ldots;\ N \geqslant r \tag{21}$$

which means that (14) is exact if γ is a positive integer and $N \geqslant \gamma - 1$.

It should be emphasised that the exactness of the phase-integral formula for diagonal matrix elements, when γ is a positive integer and $N \geqslant \gamma - 1$, previously reported for $\gamma = 1$ by Fröman *et al* (1985), is merely accidental. The total effect of other transition points than the relevant turning point x_0 is then (even for very small values of k/a) equal to zero, although the contribution from each complex transition point for small values of k/a may be considerable. According to (20) for half-integral values of γ the phase-integral formula is mediocre and even poor, if k/a is sufficiently small, and this is due to the fact that the contributions from transition points other than x_0 do not cancel one another in this case.

For complex values of γ with $|\text{Im}\ \gamma|$ too large (14) is expected to be rather mediocre as compared to the exact result in the previous section, since the phase-integral formula (A1.15) in appendix 1 is derived under the assumption that the function f is smooth.

Consider a complex value of γ with $|\mathrm{Im}\,\gamma| < k/a$, which means that the function $\exp(-\gamma a x)$ oscillates slower than the right-hand side of (7). Introducing into the right-hand side of (19) the asymptotic Tricomi–Erdélyi expansion (2.11(12)) in Luke (1969) for $\Gamma(\gamma+2ik/a)/\Gamma(1+2ik/a)$ and the same expansion for $\Gamma(\gamma-2ik/a)/\Gamma(1-2ik/a)$, we obtain

$$P(\gamma;\, k/a) \sim (2k/a)^{2\gamma-2} \sum_{n=0}^{2N} \sum_{m=0}^{2N-n} \frac{(1-\gamma)_n (1-\gamma)_m}{n!\,m!} \frac{B_n^{(\gamma)} B_m^{(\gamma)}}{(2ik/a)^n (-2ik/a)^m}$$

$$\times \left((2k/a)^{2\gamma-2} \sum_n \sum_m \frac{(1-\gamma)_n (1-\gamma)_m}{n!\,m!} \frac{B_n^{(\gamma)} B_m^{(\gamma)}}{(2ik/a)^n (-2ik/a)^m} \right)^{-1} = 1 \qquad (22)$$

the second member of (22) being exactly equal to unity, if the double sum in the denominator is truncated properly. Hence, unless $|\mathrm{Im}\,\gamma|$ is too large the phase-integral formula is very accurate, particularly if k/a is large and an optimal order of approximation is chosen.

With the aid of chapter 6 in Abramowitz and Stegun (1965) and a desk calculator one can easily show that (14) is mediocre or even poor for $|\mathrm{Im}\,\gamma| \geqslant k/a$, as compared with the exact result in § 3. Hence the function $\exp(-\gamma a x)$ should not oscillate more rapidly than $\exp(ikx)$ in order that the phase-integral formula (23) should be applicable.

The above analysis demonstrates that the rules for obtaining the region of validity of phase-integral formulae such as (A1.15) in appendix 1 are quite simple and that the phase-integral approximations are very satisfactory within their region of validity.

It should be emphasised that in practical calculations it is often sufficient to go to the third-order approximation, i.e. one chooses $N = 1$ in the formulae of this section.

5. Comparison with the corresponding phase-integral formula for non-diagonal matrix elements

For the background of the present section we refer to appendix 1. Adapting and applying (A1.16) in that appendix to the exactly soluble model described in §§ 2 and 3 with $Q(x)$ chosen according to (13) with (1*b*), we get after some calculations the phase-integral formula of order $2N+1$

$$\langle k, c|\exp(-\gamma a x)|k', c'\rangle = \tfrac{1}{2}(kk')^{1/2} \int_{(x_0)}^{+\infty} \exp(-\gamma a x)$$

$$\times \frac{\exp[\pm \mathrm{i}(w_{k,c}(x) - w_{k',c'}(x))]}{q_{k,c}^{1/2}(x)\, q_{k',c'}^{1/2}(x)}\, \mathrm{d}x \qquad \begin{cases} +\mathrm{i}, & k > k' \\ -\mathrm{i}, & k < k' \end{cases} \qquad (23)$$

where

$$w_{k,c}(x) = \sum_{n=0}^{N} w_{k,c}^{(2n+1)}(x) \qquad (24)$$

with

$$w_{k,c}^{(1)}(x) = -\frac{2}{a} R_{k,c}^{1/2}(x) + \frac{k}{a} \ln \frac{k + R_{k,c}^{1/2}(x)}{k - R_{k,c}^{1/2}(x)} \qquad (25a)$$

$$w_{k,c}^{(3)}(x) = \frac{1}{16} \frac{a}{R_{k,c}^{1/2}} - \frac{5}{48} \frac{k^2 a}{R_{k,c}^{3/2}} \qquad (25b)$$

$$w_{k,c}^{(5)}(x) = -\frac{25}{3072} \frac{a^3}{R_{k,c}^{3/2}} + \frac{531}{5120} \frac{k^2 a^3}{R_{k,c}^{5/2}} - \frac{221}{1024} \frac{k^4 a^3}{R_{k,c}^{7/2}} + \frac{1105}{9216} \frac{k^6 a^3}{R_{k,c}^{9/2}} \qquad (25c)$$

$$w^{(7)}_{k,c}(x)=\frac{1073}{163\,840}\frac{a^5}{R^{5/2}_{k,c}}-\frac{50\,049}{229\,376}\frac{k^2a^5}{R^{7/2}_{k,c}}+\frac{186\,821}{147\,456}\frac{k^4a^5}{R^{9/2}_{k,c}}$$
$$-\frac{44\,899}{16\,384}\frac{k^6a^5}{R^{11/2}_{k,c}}+\frac{82\,825}{32\,768}\frac{k^8a^5}{R^{13/2}_{k,c}}-\frac{82\,825}{98\,304}\frac{k^{10}a^5}{R^{15/2}_{k,c}} \tag{25d}$$

and where

$$q_{k,c}(x)=\frac{\mathrm{d}w_{k,c}(x)}{\mathrm{d}x}. \tag{26}$$

The notations are essentially the same as in appendix 1, although adapted to the present one-dimensional problem and with the dependence on k and c indicated in an obvious way (see figure 1). According to p 755 in Fröman *et al* (1979), in the exponential function in the numerator of the above formula (23) the plus sign should be used if $k>k'$, while the minus sign should be used if $k<k'$. The dependence of R on k and c is indicated explicitly in the notation.

The explicit expression for the function $q_{k,c}(x)$ in (23) in the order $2N+1$ is obtained after some calculation as

$$q_{k,c}(x)=R^{1/2}_{k,c}(x)\sum_{n=0}^{N}Y_{2n} \tag{27}$$

where

$$Y_0=1 \tag{28a}$$

$$Y_2=\frac{a^2}{32R_{k,c}}-\frac{3k^2a^2}{16R^2_{k,c}}+\frac{5k^4a^2}{32R^3_{k,c}} \tag{28b}$$

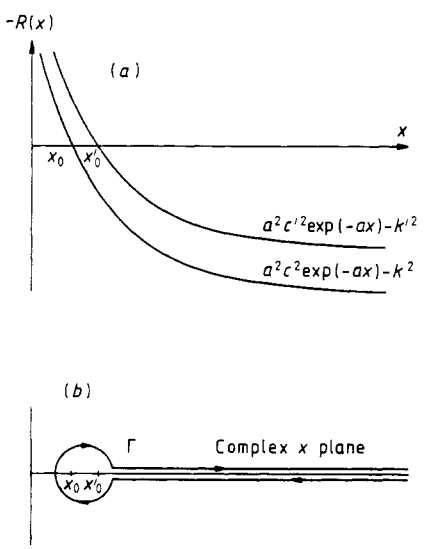

Figure 1. (*a*) shows $-R_{k,c}(x)$ and $-R_{k',c'}(x)$ for $k\neq k'$ (and possibly $c\neq c'$). The classical turning points are denoted by x_0 and x'_0, respectively. (*b*) shows the contour of integration Γ in the phase-integral formula (23) for quantal matrix elements associated with non-bound states, where it should be noted that $\int_{(x_0)}^{+\infty}\ldots\mathrm{d}x=\frac{1}{2}\int_{\Gamma}\ldots\mathrm{d}x$. This contour shall enclose both classical turning points x_0 and x'_0. The function $R^{1/2}(x)$ is positive on the upper lip of the cut emerging from x_0 and x'_0 to the right along the real axis, provided c is real.

$$Y_4 = -\frac{25a^4}{2048R_{k,c}^2} + \frac{139k^2a^4}{512R_{k,c}^3} - \frac{1039k^4a^4}{1024R_{k,c}^4} + \frac{663k^6a^4}{512R_{k,c}^5} - \frac{1105k^8a^4}{2048R_{k,c}^6} \tag{28c}$$

$$Y_6 = \frac{1073a^6}{65\,536R_{k,c}^3} - \frac{25\,561k^2a^6}{32\,768R_{k,c}^4} + \frac{423\,691k^4a^6}{65\,536R_{k,c}^5} - \frac{340\,355k^6a^6}{16\,384R_{k,c}^6} + \frac{2064\,503k^8a^6}{65\,536R_{k,c}^7} - \frac{745\,425k^{10}a^6}{32\,768R_{k,c}^8} + \frac{414\,125k^{12}a^6}{65\,536R_{k,c}^9}. \tag{28d}$$

Let us now particularise to the case $c' = c$. Since according to (1*b*) we have

$$R_{k',c}(x) = k'^2 - k^2 + R_{k,c}(x) \tag{29}$$

$$\exp(-\gamma a x) = c^{-2\gamma}(k^2 - R_{k,c}(x))^{\gamma} a^{-2\gamma} \tag{30}$$

and

$$\mathrm{d}x = \frac{\mathrm{d}R_{k,c}}{a(k^2 - R_{k,c})} \tag{31}$$

it is easily seen from (23) with (24), (25) and (26) that the right-hand side of (23) can be rewritten as $c^{-2\gamma}$ multiplied by a c-independent integral over $R_{k,c}$ with 'lower limit' 0 (since $R_{k,c}(x_0) = 0$) and upper limit k^2. Hence, for $c' = c$ the only dependence of c of the right-hand side of (23) is due to a factor $c^{-2\gamma}$ (cf also equation (14) in § 4), which is the same c dependence as is found in the exact matrix element (12) or (12′) with $c' = c$. Hence the error of the phase-integral approximation is independent of c (real or complex) and the error analysis can therefore be restricted to real values of c when $c' = c$ (and even to $c = 1$).

The evaluation of the non-diagonal matrix elements by means of the phase-integral formula (23) is most conveniently carried out with the aid of a computer program, which allows the calculations to be carried out rather automatically. The results of the numerical calculations for comparing the phase-integral results obtained from (23) with the exact results obtained from (12) are shown in figure 2 for various values of Im γ. The relative error of the phase-integral formula (23) given in this figure was

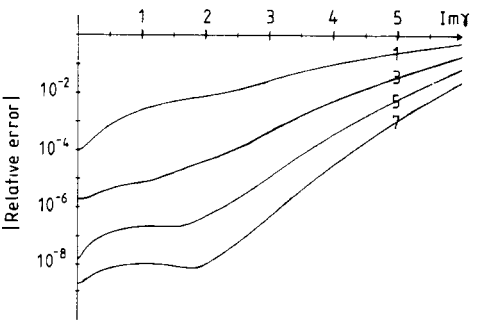

Figure 2. For $a = 1$, $c = c' = \mathrm{Re}\,\gamma = 1$, $k = 5$, $k' = 2.5$ this figure gives the absolute value of the relative error (32) of the phase-integral value of the matrix element, obtained from (23), as a function of Im γ. The figures (1, 3, 5, 7) at the curves indicate the orders of the phase-integral approximation. The figure confirms that accurate results are obtained if the function $\exp(-\gamma a x)$ does not oscillate too strongly. The figure also illustrates that the phase-integral formula gives mediocre or poor accuracy for Im $\gamma > \max(k'/a, k/a)$.

obtained by first subtracting the exact value from the phase-integral value, dividing this difference by the exact value and finally taking the absolute value:

|the relative error|

$$= \left| \frac{\langle k,c|\exp(-\gamma ax)|k',c'\rangle_{\text{approx}} - \langle k,\, c|\exp(-\gamma ax)|k',\, c'\rangle_{\text{exact}}}{\langle k,\, c|\exp(-\gamma ax)|k',\, c'\rangle_{\text{exact}}} \right| . \tag{32}$$

Figure 2 shows that the phase-integral results for the off-diagonal matrix elements obtained from (23) are very accurate for small values of $|\text{Im}\ \gamma|$ and are reasonably accurate up to $|\text{Im}\ \gamma| = \max(k/a, k'/a)$. Hence, the function $\exp(-\gamma ax)$ should not oscillate more rapidly than $\exp(ikx)$ if $k > k'$ in order that the phase-integral formula (23) should be applicable.

6. Concluding remarks

An exact formula for the matrix element

$$\langle k,\, c|\exp(-\gamma ax)|k'c'\rangle = \langle k,\, c|\exp(-\alpha ax - i\beta ax)|k',\, c'\rangle$$

where $\text{Re}\ c > 0$, $\text{Re}\ c' > 0$, $\alpha > 0$ and β is real, has been derived for the case of an exponential potential. The respective potential is $\exp(-ax)a^2c^2\hbar^2/2m$ with energy $\hbar^2k^2/2m > 0$ and $\exp(-ax)a^2c'^2\hbar^2/2m$ with energy $\hbar^2k'^2/2m > 0$. By taking the real part and the imaginary part respectively, we obtain for real values of c and c' the matrix elements

$$\langle k,\, c|\exp(-\alpha ax)\cos(\beta ax)|k',\, c'\rangle$$

and

$$\langle k,\, c|\exp(-\alpha ax)\sin(\beta ax)|k',c'\rangle.$$

It should be useful, for various practical purposes, to have such an exact expression for the respective matrix element.

During the present investigation the authors have also considered the effective extension to the $l \neq 0$ case. This cannot be done in a simple way for the purely exponential potential. However, an exactly soluble model of a screened Coulomb potential, for which the matrix element of $\exp(-\gamma ax)$ between states with different l can be obtained exactly, has been reported by Myhrman (1983) for the case of bound states and positive real values of γ. It should be possible to extend Myhrman's (1983) investigation to the case of unbound states and complex γ with $\text{Re}\ \gamma > 0$.

In most applications, however, one must rely upon approximate calculations. For matrix element calculations brute force computing may raise difficulties, particularly if the wavefunction oscillates rapidly. Fröman *et al* (1979) have obtained a formula for the matrix element of a smooth function between unbound states for a one-turning-point (one-dimensional or radial) problem. The exact formula in the present paper has been used to test the formula obtained by Fröman *et al* (1979).

Our investigation has shown that the phase-integral formula for the matrix element is very satisfactory for a one-turning-point problem, as long as the function $\exp(-\gamma ax) = \exp(-\alpha ax - i\beta ax)$ does not oscillate too strongly. It should be noted, however, that for a given potential, such as the exponential potential, for sufficiently low energies there may appear extra (possibly complex) transition points, the contribu-

tions of which cannot be neglected. In a previous study of the phase-integral matrix element of $\exp(-ax)$ by Fröman *et al* (1985) using the Jackson-Mott formula this effect from the extra transition points accidentally did not show up. This can be understood in the following way. For low energies in the Jackson-Mott case ($\gamma = 1$ in the present work) there is a contribution from each extra complex transition point. Each such contribution is significant for low energies also when $\gamma = 1$ but the total effect accidentally vanishes completely also for low energies.

We have demonstrated that the phase-integral diagonal and non-diagonal matrix elements of a function corresponding to a smooth or rather smooth damped oscillation are very accurate, provided a one-turning-point problem is considered. For a function which oscillates too strongly, however, the accuracy becomes rather mediocre and even poor. This is in agreement with bound-state matrix element results (for $\exp(ikx)$ between harmonic oscillator states) reported by Fröman and Fröman (1977). Quantitatively we find that the function in the matrix element should not oscillate more rapidly than the wavefunction involved, which oscillates most rapidly.

In the present investigation we have only been able to present very limited numerical material. However, there exists at our institute a numerical program with the aid of which the phase-integral calculations can be performed in a rather automatic way, and this program can be made available to potential users.

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Appendix 1. Brief description of the arbitrary-order phase-integral approximation and of phase-integral formulae for matrix elements between unbound states

According to the phase-integral approximation of the order $2N+1$, introduced by Fröman (1966, 1970) and generalised, for example, by Fröman and Fröman (1974), the differential equation (1*a*), i.e.

$$\mathrm{d}^2u/\mathrm{d}x^2 + R(x) = 0 \tag{A1.1}$$

has the two linearly independent approximate solutions (cf equation (8) in Fröman and Fröman 1974)

$$u = q^{-1/2}(x)\exp(\pm \mathrm{i}w(x)) \tag{A1.2}$$

where

$$w(x) = \int^x q(x)\,\mathrm{d}x \tag{A1.3}$$

and

$$q(x) = \sum_{n=0}^{N} Y_{2n}Q(x). \tag{A1.4}$$

Here $Q(x)$ is an unspecified function, called the *base function*, which can be chosen conveniently, and the first few of the quantities Y_{2n} are (cf equations (6*a*)-(6*d*) in Fröman and Fröman (1970))

$$Y_0 = 1 \tag{A1.5a}$$

$$Y_2 = \tfrac{1}{2}\varepsilon_0 \tag{A1.5b}$$

$$Y_4 = -\tfrac{1}{8}(\varepsilon_0^2 + \varepsilon_2) \tag{A1.5c}$$

$$Y_6 = \tfrac{1}{32}(2\varepsilon_0^3 + 5\varepsilon_1^2 + 6\varepsilon_0\varepsilon_2 + \varepsilon_4) \tag{A1.5d}$$

where (cf equation (3) in Fröman and Fröman (1974))

$$\varepsilon_0 = \frac{R(x) - Q^2(x)}{Q^2(x)} + Q^{-3/2}(x)\frac{\mathrm{d}^2}{\mathrm{d}x^2}Q^{-1/2}(x) \tag{A1.6}$$

and (cf Fröman and Fröman 1974)

$$\varepsilon_\mu = \frac{1}{Q(x)}\frac{\mathrm{d}}{\mathrm{d}x}\varepsilon_{\mu-1} \qquad \mu \geqslant 1. \tag{A1.7}$$

The advantage of using the phase-integral approximation described above instead of the JWKB approximation, when a higher-order approximation is needed, is described in the appendix of Fröman and Fröman (1985). The choice of the unspecified base function $Q(x)$, appearing in the phase-integral approximation, is also discussed in that appendix.

For the higher orders of the phase-integral approximation the function $q(x)$ has such strong singularities at the points where $Q^2(x)$ has zeros that one cannot choose the constant lower limit of integration on the right-hand side of the definition (A1.3) of $w(x)$ to be a zero of $Q^2(x)$, which is often convenient when the first-order approximation is used. When $Q^2(x)$ has a simple zero, and an arbitrary order of the approximation is used, it is instead often convenient to write $w(z)$ as a certain contour integral on a two-sheet Riemann surface on which $q(x)$ is single valued. The two sheets of this Riemann surface are cut and joined appropriately along a line emerging from the zero x_0 of $Q^2(x)$ in question. Thus one defines

$$w(x) = \int_{(x_0)}^{x} q(x)\,\mathrm{d}x \tag{A1.8}$$

with

$$\int_{(x_0)}^{x} q(x)\,\mathrm{d}x = \tfrac{1}{2}\int_{\Gamma(x)} q(x)\,\mathrm{d}x \tag{A1.9}$$

where $\Gamma(x)$ is a contour of integration starting at the point corresponding to x but lying on the next (or on the previous) Riemann sheet encircling the zero x_0 of $Q^2(x)$ in the negative (or in the positive) sense, and ending at the point x. Such a contour $\Gamma(x)$ in the limit as x tends to $+\infty$, with the turning point encircled in the negative sense, is shown in figure 1(*b*). For the first-order approximation the contour $\Gamma(x)$ can be deformed such that the integral (A1.8) goes over into an integral from x_0 to x, and hence $w(x)$, originally defined by (A1.8) with (A1.9) is in this particular case also given by the integral in the right-hand member of (A1.3) with the generalised classical turning point, i.e. the zero x_0 of $Q^2(x)$, as the lower limit of integration. When $R(x)$ and $Q^2(x)$ are real on the real x axis, the functions Y_{2n} are real there, and hence, on

the real x axis, the function $w(x)$, given by (A1.8), is (for any order of approximation) real on the side of the generalised turning point where $Q^2(x)$ is positive (classically allowed region in the generalised sense) but purely imaginary on the side of the generalised turning point where $Q^2(x)$ is negative (classically forbidden region in the generalised sense).

Now we shall consider, in a radial (spherically symmetric) effective potential, a non-bound state with a single generalised turning point x_0. The state is characterised by the orbital angular momentum l and the radial momentum $\hbar k$ (at infinitely large distance from the centre of force). In the definition of the matrix element of $f(x)$, involving two unbound states,

$$\langle l, k|f(x)|l', k'\rangle = \int_0^\infty u_{l,k}(x) f(x) u_{l',k'}(x)\, \mathrm{d}x. \tag{A1.10}$$

We normalise $u_{l,k}(x)$ (and similarly $u_{l',k'}(x)$) by requiring that

$u_{l,k}(x)$ shall for a real potential be positive immediately to the right of $x=0$ (A1.11a)

and

$$u_{l,k}(x) \sim \sin(kx - l\pi/2 + \delta_l) \qquad x \to +\infty \tag{A1.11b}$$

where δ_l is the asymptotic scattering phase shift.

According to (A1.16) in the appendix of Fröman *et al* (1985) we have the approximate formula for the diagonal matrix element

$$\langle l, k|f(x)|l, k\rangle = \tfrac{1}{2}k \int_{(x_0)}^{+\infty} f(x) \sum_{n=0}^{N} C_{2n} \frac{\mathrm{d}x}{Q_{l,k}(x)} \tag{A1.12}$$

where the integration symbol is explained above in connection with (A1.9), and where the first few of the quantities C_{2n} are given by equations (22a)-(22d) in Fröman (1974), i.e.

$$C_0 = Y_0 = 1 \tag{A1.13a}$$

$$C_2 = -Y_2 \tag{A1.13b}$$

$$C_4 = -(Y_4 - Y_2^2) \tag{A1.13c}$$

$$C_6 = -(Y_6 - 2Y_2Y_4 + Y_2^3). \tag{A1.13d}$$

When x does not lie too close to a zero or singularity of $Q^2(x)$, the quantities $Y_2, Y_4, Y_6, \ldots$, should be small compared to unity, and by means of (A1.4) and (A1.13a)-(A1.13d) we obtain the approximate formula (cf equation (25) in Fröman 1974)

$$\frac{1}{Q(x)} \sum_{n=0}^{N} C_{2n} = \frac{1}{q(x)}. \tag{A1.14}$$

Inserting (A1.14) into (A1.12), we obtain the approximate but often very accurate phase-integral formula for the diagonal matrix element

$$\langle l, k|f(x)|l, k\rangle = \tfrac{1}{2}k \int_{(x_0)}^{+\infty} f(x) \frac{\mathrm{d}x}{q(x)}. \tag{A1.15}$$

The generalisation of (A1.15) to non-diagonal matrix elements is according to equation (A.17) in the appendix of Fröman *et al* (1985) or equation (14) in Fröman *et al* (1979)

$$\langle l, k|f(x)|l', k'\rangle = \tfrac{1}{2}(kk')^{1/2}\int_{(x_0)}^{+\infty} f(x)\frac{\exp[\pm \mathrm{i}(w_{l,k}(x)-w_{l',k'}(x))]}{q_{l,k}^{1/2}(x)q_{l',k'}^{1/2}(x)}\,\mathrm{d}x \tag{A1.16}$$

where both states are assumed to be unbound, and (unless the difference $l-l'$ is positive and too large) the plus sign should be used if $k>k'$, while the minus sign should be used if $k<k'$, and where the path of integration should follow the contour Γ in figure 1(*b*) with due care taken to the factor $\frac{1}{2}$ in our integration symbol; cf (A1.9) above. For the case when both states are bound or one state bound and one unbound, cf the appendix in Fröman *et al* (1985).

Appendix 2. Alternative derivation of the exact quantal matrix element

We shall now demonstrate a procedure, alternative to the one in § 3, for obtaining the matrix element $\langle k, c|\exp(-\gamma a x)|k', c'\rangle$ with $c'=c$. The derivation may be of some use, for example in connection with generalisations. Substituting (4) into (8) and introducing into the resulting formula the substitution (10) we obtain

$$\begin{aligned}\langle k, c|\exp(-\gamma a x)|k', c'\rangle &= (2\pi^2 a)^{-1}[(2\pi k/a)\sinh(2\pi k/a)(2\pi k'/a)\sinh(2\pi k'/a)]^{1/2}2^{-2\gamma}\\ &\times\int_0^{\infty}\mathrm{d}z\, z^{2\gamma-1}\int_{-\infty}^{+\infty}\mathrm{d}y\int_{-\infty}^{+\infty}\mathrm{d}y'\\ &\times\exp[-z(c\cosh y + c'\cosh y')]\cos(2ky/a)\cos(2ky'/a).\end{aligned} \tag{A2.1}$$

Interchanging the orders of the integrations in (A2.1) so that the integration with respect to z is performed first, we obtain with the aid of Euler's integral for the gamma function (cf equation (6.1.1) in Abramowitz and Stegun (1965))

$$\begin{aligned}\langle k, c|\exp(-\gamma a x)|k', c'\rangle &= (2\pi^2 a)^{-1}[(2\pi k/a)\sinh(2\pi k/a)(2\pi k'/a)\sinh(2\pi k'/a)]^{1/2}\\ &\times\Gamma(2\gamma)\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{\cos(2ky/a)\cos(2k'y'/a)}{(c\cosh y + c'\cosh y')^{2\gamma}}\,\mathrm{d}y\,\mathrm{d}y'.\end{aligned} \tag{A2.2}$$

Introducing the new variables of integration

$$t = \tfrac{1}{2}(y+y') \tag{A2.3a}$$

$$t' = \tfrac{1}{2}(y-y') \tag{A2.3b}$$

and using the identities

$$\cosh(t+t')+\cosh(t-t') = 2\cosh t\cosh t' \tag{A2.4a}$$

$$\begin{aligned}2\cos[2k(t+t')/a]\cos[2k'(t-t')/a] &= \cos[2(k+k')t/a]\cos[2(k-k')t'/a]\\ &+\cos[2(k+k')t'/a]\cos[2(k-k')t/a]\\ &-\sin[2(k+k')t/a]\sin[2(k-k')t'/a]\\ &-\sin[2(k+k')t'/a]\sin[2(k-k')t/a]\end{aligned} \tag{A2.4b}$$

we obtain from (A2.2) with $c' = c$ after some calculations

$$\langle k, c|\exp(-\gamma a x)|k', c\rangle = (\pi^2 a)^{-1}[(2\pi k/a)\sinh(2\pi k/a)(2\pi k'/a)\sinh(2\pi k'/a)]^{1/2}$$
$$\times (4c)^{-2\gamma}\Gamma(2\gamma)\int_{-\infty}^{+\infty}\frac{\cos[2(k+k')t/a]}{(\cosh t)^{2\gamma}}\,\mathrm{d}t$$
$$\times\int_{-\infty}^{+\infty}\frac{\cos[2(k-k')t'/a]}{(\cosh t')^{2\gamma}}\,\mathrm{d}t'. \tag{A2.5}$$

Evaluating each integral in (A2.5) with the aid of equation (3.985) in Gradshteyn and Ryshik (1980), we obtain

$$\langle k, c|\exp(-\gamma a x)|k', c\rangle$$
$$= (4\pi^2 a)^{-1}[(2\pi k/a)\sinh(2\pi k/a)(2\pi k'/a)\sinh(2\pi k'/a)]^{1/2}c^{-2\gamma}$$
$$\times\Gamma(\gamma+\mathrm{i}(k'+k)/a)\Gamma(\gamma+\mathrm{i}(k'-k)/a)\Gamma(\gamma-\mathrm{i}(k'+k)/a)$$
$$\times\Gamma(\gamma-\mathrm{i}(k'-k)/a)/\Gamma(2\gamma) \tag{A2.6}$$

which is valid under the assumptions (2*a*, *b*) and (9). Putting $\gamma = 1$, and using equation (6.1.31) in Abramowitz and Stegun (1965) we obtain from (A2.6) the Jackson-Mott (1932) formula as a particular case.

References

Abramowitz M and Stegun I A (ed) 1965 *Handbook of Mathematical Functions* (Washington, DC: NBS)
Eno L and Balint-Kurti G G 1977 *Chem. Phys.* **23** 295
Erdélyi A (ed) 1953 *Tables of Integral Transforms* vol II (New York: McGraw-Hill)
Fröman N 1966 *Ark. Fys.* **32** 541
—— 1970 *Ann. Phys., NY* **61** 451
Fröman N and Fröman P O 1970 *Nucl. Phys.* A **147** 606
—— 1974 *Ann. Phys., NY* **83** 103
—— 1977 *J. Math. Phys.* **18** 903
—— 1985 *Ann. Phys., NY* **163** 215
Fröman N, Fröman P O and Karlsson F 1979 *Mol. Phys.* **38** 749
Fröman P O 1974 *Ann. Phys., NY* **88** 621
Fröman P O, Hökback A, Walles E and Yngve S 1985 *Ann. Phys., NY* **163** 252
Gradshteyn I S and Ryshik I M 1980 *Tables of Integrals, Series and Products* (New York: Academic)
Jackson J M and Mott N F 1932 *Proc. R. Soc.* A **137** 703
Luke Y L 1969 *The Special Functions and Their Approximations* vol I (New York: Academic)
Mies F H 1964 *J. Chem. Phys.* **40** 523
Myhrman U 1983 *J. Phys. A: Math. Gen.* **16** 263