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Comments

Comment on the Discrepancy between the Jackson and Mott Transition Probability and the Exact Calculation of Secrest and Johnson*

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Exact calculations for the collinear collision of a particle with a harmonic oscillator[1] have shown, perhaps unexpectedly, that the Jackson and Mott (JM) formula[2] is in disagreement with the exact one, even for very low transition probabilities. This is where one would have expected the JM treatment to be most accurate. The purpose of this Comment is to show that part of this difference is due to the fact that the JM approximation is not identical to a true distorted wave (DW) treatment and that the approximation made in obtaining the JM formula from the distorted wave equations is not valid even for harmonic oscillators. Since the difference between the JM and DW method has been discussed in detail by Mies,[3] we shall simply outline the basic results.

The JM formula is obtained from the DW equations by assuming the diagonal matrix elements are identical;

$$V_{nn}/V_{jj}=1, \qquad (1)$$

where $V_{nn}=\langle n \mid V \mid n \rangle$, V is the interaction potential of the particle with the oscillator, which in this case is an exponential interaction, and n (or j) represents the state of the oscillator. Mies pointed out, however, that a small deviation from (1) could produce a very large error in the transition probabilities for anharmonic oscillators as described by Morse functions. It is this same effect which accounts for much of the difference between the JM and the exact transition probabilities, calculated by Secrest and Johnson.

Calculations were performed for the 0→1 transition taking cognizance of the fact that $V_{00} \neq V_{11}$. The results are given in Table I and compared with the exact and the JM results. In every case there is a significant improvement of the DW calculation over the JM. In

TABLE I. Transition probabilities for the Harmonic oscillator (0→1).

E_{total}[a]	P_{exact}	P_{DW}	P_{JM}
$m=0.5$	$\alpha=0.114$	$V_{11}/V_{00}=1.0065$	
7.6	4.30×10^{-5}	5.88×10^{-5}	1.00×10^{-4}
8.8	2.03×10^{-4}	2.76×10^{-4}	4.71×10^{-4}
10.0	6.58×10^{-4}	9.01×10^{-4}	1.53×10^{-3}
12.0	2.85×10^{-3}	3.88×10^{-3}	6.64×10^{-3}
16.0	1.92×10^{-2}	2.65×10^{-2}	4.52×10^{-2}
20.0	6.39×10^{-2}	9.00×10^{-2}	1.55×10^{-1}
$m=0.2$	$\alpha=0.114$	$V_{11}/V_{00}=1.0065$	
6.0	7.06×10^{-4}	8.05×10^{-4}	9.78×10^{-4}
10.0	2.82×10^{-2}	3.19×10^{-2}	3.92×10^{-2}
14.0	1.32×10^{-1}	1.58×10^{-1}	1.97×10^{-1}
18.0	2.88×10^{-1}	4.14×10^{-1}	5.12×10^{-1}
20.0	3.56×10^{-1}	5.91×10^{-1}	7.31×10^{-1}
$m=1.25$	$\alpha=0.2973$	$V_{11}/V_{00}=1.0442$	
4.9455	1.12×10^{-4}	2.79×10^{-4}	1.19×10^{-3}

[a] E_{total}, m, and α are the total energy, reduced mass, and potential parameter as defined by Secrest and Johnson.

contradiction to a statement in the recent review article by Takayanagi,[4] we can conclude that, even for the case of simple harmonic oscillators, a large part of the discrepancy between the JM and the exact treatments for low transition probabilities is due to $V_{nn}=V_{jj}$ not being a valid approximation.

[1] D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966).
[2] J. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) **A137**, 703 (1932).
[3] F. H. Mies, J. Chem. Phys. **40**, 523 (1964).
[4] K. Takayanagi, *Advances in Atomic and Molecular Physics*, D. R. Bates and I. Estermann, Eds. (Academic Press Inc., New York, 1965), Vol. 1.

Energy Transfer in the Distorted Wave Approximation*

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In the preceding Comment,[1] Roberts shows that the true distorted wave approximation is superior to

TABLE I.[a] Energy transfer in the
Mott and Jackson approximation.

E	$P_{0\to1}^{MJ}/P_{0\to1}$	$P_{0\to1}^{MJ}$	$P_{0\to1}^{MJ}/\sum_n nP_{0\to n}$
6	3.19	0.07	3.19
8	3.28	0 4	3.22
10	3.63	0.9	3.24
12	4.44	1.7	3.31
16	9.47	4.1	3.34
20	32.9	7.2	3.40

[a] All data for this table are in Ref. 6.

the Mott and Jackson[2] approximation. This brings the distorted wave approximation for vibrational energy transfer more into line with that for rotational[3] energy transfer. The ratio of the rotational transition cross sections in the distorted wave approximation to the exact quantities varies from unity by about 20%.

If one computes the ratio of the true distorted wave energy transfer as given by Roberts to the exact energy transfer, a constant is obtained throughout the entire range of energy considered. The exact classical mechanical solutions of Kelly and Wolfsberg[4] were also in a constant ratio to the approximate solution of Rapp[5] and the ratio of the approximate classical to the exact classical is the same as the ratio of the Mott and Jackson approximation to the exact quantum mechanical.[6] In the approximate classical calculation, Rapp expanded the exponential in the interaction potential and carried only one term. This may be the approximation which makes the classical Rapp approximation equivalent to the Mott and Jackson approximation.

It is interesting to note that while the Mott and Jackson approximation for the transition probability becomes very bad at high energies, giving excitation probabilities greater than one, if it is used to compute energy transfer, it is only very little worse at these high energies than at very low energies, in many cases.

In Table I we give the ratio of energy transfer in the Mott and Jackson approximation, $2P_{0\to1}^{MJ}$, to the exact energy transfer $2\sum_n nP_{0\to n}$. The ratio is only slightly larger at $E=20$ than at $E=6$, though $P_{0\to1}^{MJ}=7.2$ at the high-energy end. It would be interesting to see if the true distorted wave calculation held as constant a ratio at high energies.

In the Roberts calculation, the ratio of energy transfers is constant for the two examples given.

[1] R. E. Roberts, J. Chem. Phys. **48**, 2880 (1968) (previous letter).
[2] J. M. Jackson and N. F. Mott, Proc. Roy. Soc. (London) **A137**, 703, (1932).
[3] B. R. Johnson and D. Secrest, J. Chem. Phys. **48**, 4682 (1968).
[4] J. D. Kelley and M. Wolfsberg, J. Chem. Phys. **44**, 324 (1966).
[5] D. Rapp, J. Chem. Phys. **32**, 735 (1960).
[6] D. Secrest and B. R. Johnson, J. Chem. Phys. **45**, 4556 (1966).

Errata

Erratum: The Growth and Decay of Delayed Luminescence

[J. Chem. Phys. **48**, 1924 (1968)]

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In an earlier paper[1] we noted that the difference between the growth and decay rate constants of the phosphorescence of organic solutes in glassy media (i.e., $K_p^R - K_p^D$) was attributable to ground-state (S_0) depletion and triplet–triplet absorption ($T_j\leftarrow T_1$) processes. In our last paper[2] on this topic we implicated $T_j\leftarrow T_1$ processes solely. We wish now to point out that this latter attribution was incorrect and that $K_p^R - K_p^D$ differences are almost wholly due to ground-state depletion effects.

If Eqs. (1)–(5) of the previous paper[2] are retained, if the ground-state concentration $[S_0]$ is made time dependent and written as $[S_0]=\eta-[S_1]-[T_1]$, where η is the total solute concentration, and if we designate ρ as the rate constant for the $S_1\leftarrow T_1$ process initiated by $T_j\leftarrow T_1$ absorption, we find

$$[S_0]=\eta\{1-[E_0(K_2+K_3+\rho)/\lambda_1\lambda_2][1-\exp(-t/\tau_p^R)]\},$$
$$(1)$$

$$[T_1]=(\eta E_0K_2/\lambda_1\lambda_2)[1-\exp(-t/\tau_p^R)], \quad (2)$$

where

$$1/\tau_p^R=K_3+\rho+[K_2(E_0-\rho)]/(E_0+K_1+K_2-K_3-\rho)$$

and

$$\lambda_1\lambda_2=[(E_0+K_1+K_2)(K_3+\rho)+K_2(E_0-\rho)].$$

Equation (2), in conjunction with the normal phosphorescence decay expression,[2] yields

$$K_p^R-K_p^D=\rho+[K_2(E_0-\rho)]/(E_0+K_1+K_2-K_3-\rho).$$
$$(3)$$