THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 10 15 NOVEMBER 1968

Classical Mechanics of Rotational–Translational and Other Energy Transfer. I. A Hamilton–Jacobi (Action-Angle) Treatment*

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(Received 22 July 1968)

The classical-mechanical equations of motion describing collisional energy transfer are converted to a form involving constants of the elastic collision, using a Hamilton–Jacobi formalism. These constants frequently vary only slowly during an inelastic collision. An approximate version of the transformed equations, related to a variation of constants procedure, is next introduced. The collision of an atom with a rigid linear diatomic molecule is considered in some detail. Several desirable features of the approximation are that the change in rotational angular momentum is obtained directly, all initial orientations of particles and angular momenta occur outside the integrals, an approximate error estimate can be made, results can be calculated relatively quickly, and further insight is obtained into the energy-transfer process. Because of the close relationship of Hamilton–Jacobi and Schrödinger formalisms, a comparison of exact and approximate classical results is also expected to provide estimates of range of validity of some commonly used approximations in the quantum case.

INTRODUCTION

Recently, classical-mechanical rotational energy transfer has been used to develop several approximate expressions for rotational relaxation times and to calculate cross sections related to spectral band contours and relaxation times: The rotational relaxation problem was treated in two dimensions using approximate[1,2] and exact (numerical)[3] integration of the equations of motion. Further, classical cross sections in three dimensions have been introduced into an extension[4] of an impact theory[5] for relaxation times for microwave, infrared, Raman, and nuclear spin spectra. They have also been introduced in autocorrelation function expressions for fluorescence depolarization, pressure, and frequency dependence of nonresonant microwave absorption, and sound absorption.[6]

These relaxation times and cross sections for rotational energy transfer are obtained by averaging quantities such as the square of the change in rotational energy[1] or the transition probability[4,6] over the appropriate phase space. Normally, the averaging process necessitates either major approximations[1,2,7] or many integrations of the exact, classical equations of motion.[3,4,6] Two very interesting approximations have been proposed to reduce the number of coupled differential equations involved for a classical inelastic collision,[8] and an approximate solution has been derived for large impact parameters.[9]

The present paper makes use of techniques which have been employed to advantage in celestial mechanics.[10] In particular, we first solve[11] the Hamilton–Jacobi equation for the elastic collision. The latter yields a contact transformation which converts the equations of motion for the perturbed problem (i.e., the inelastic problem) to a more convenient form. The convenience arises because the constants of the motion for an elastic collision become, frequently, only slowly varying functions of time for an inelastic collision. As in celestial mechanics the resulting equations can be used for numerical or more approximate solution. A Hamilton–Jacobi formalism has also been used by one of us to treat reactive collisions.[12]

An approximate solution of the resulting exact equations is next given. It has a number of desirable features: (1) Δj, the change in rotational angular momentum, is obtained directly, (2) all initial angular orientations of the particles and their angular momenta occur outside the integrals, (3) an approximate error estimate can be made, (4) results can be calculated relatively quickly, and (5) further insight is obtained into the process of rotational energy transfer. This approximate solution works best for collisions involving closely spaced rotational energy levels[13] and moderately anisotropic potential-energy functions.

For ease of presentation, we first describe the applica-

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* Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

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[12] R. A. Marcus, J. Chem. Phys. 45, 4500 (1966); 49, 2617 (1968) (Part IV).

[13] Since systems with many closely spaced rotational energy levels are difficult to treat quantum mechanically or semiclassically, it is fortunate that the approximate solution works best for these systems.

tion of the method to the rotational–translational energy transfer problem in three dimensions for an atom colliding with a rigid linear molecule and then indicate the appropriate modifications for treating more complex problems involving rotational–vibrational–translational energy transfers in polyatomic systems. Because of the close relation of Hamilton–Jacobi and Schrödinger formalisms, a comparison of approximate with exact classical results is expected to provide some estimate of the range of validity of some commonly used approximations in the quantum case, a matter considered further in a later paper.

COLLISION OF AN ATOM WITH A RIGID ROTOR

The Hamiltonian for the collision of an atom and a rigid linear molecule is described by the familiar Hamiltonian

$$H=(2\mu)^{-1}\left[p_R^2+\frac{1}{R^2}\left(p_\Theta^2+\frac{p_\Phi^2}{\sin^2\Theta}\right)\right]$$

$$+\frac{1}{2\mu_m r^2}\left(p_\theta^2+\frac{p_\phi^2}{\sin^2\theta}\right)+V(R,\gamma). \quad (1)$$

Here, R, Θ, and Φ are the spherical polar coordinates of the vector **R** from the center of mass of the atom to the center of mass of the molecule. γ is the angle describing the orientation of the molecule relative to **R**. p_R, p_Θ, and p_Φ are conjugate to R, Θ, Φ. r, θ, and ϕ are the spherical polar coordinates of the axis of the rotor, while p_θ and p_ϕ are the momenta conjugate to θ and ϕ. μ_m is the reduced mass of the linear molecule,[14] and μ is the reduced mass for the atom–molecule collision.

The Hamiltonian (9) can be written as

$$H=H_0+V_p, \quad (2)$$

where H_0 is H with $V(R,\gamma)$ replaced by its spherically averaged value V_0,

$$V_0(R)=\frac{1}{2}\int_0^\pi V(R,\gamma)\sin\gamma d\gamma, \quad (3)$$

and V_p is the asymmetric contribution to $V(R,\gamma)$,

$$V_p(R,\gamma)=V(R,\gamma)-V_0(R). \quad (4)$$

The Hamilton–Jacobi equation for the elastic collision is obtained by replacing each p_i in H_0 by $\partial W(\alpha_i, q^i)/\partial q^i$, where $W(\alpha_i, q^i)$ is the unknown generating function and the α_i are constants of the motion for an elastic collision, and then setting H_0 equal to E, the total energy. Solution of this equation by separation of variables introduces separation constants[15] l, m_l, j, and m_j and yields[11,16] Eq. (5) for W

$$W(q^i;\alpha_i)=W_I(\Theta,\Phi,\theta,\phi;l,m_l,j,m_j)+W_R, \quad (5)$$

where[17]

$$W_I=m_l\Phi+m_j\phi+\int(l^2-m_l\csc^2\Theta)^{1/2}d\Theta$$

$$+\int(j^2-m_j^2\csc^2\theta)^{1/2}d\theta \quad (6)$$

and

$$W_R=\int\left[2\mu\left(E-\frac{l^2}{2\mu R^2}-\frac{j^2}{2\mu_m r^2}-V_0\right)\right]^{1/2}dR. \quad (7)$$

A second useful generating function is obtained by replacing W_R by the one[18] for an identity transformation, yielding

$$W=W_I+\bar{p}_R R, \quad (8)$$

where $\bar{p}_R$ is the new momentum conjugate to R.

In either case W is $W(P_i, q^i)$, where the P_i are the new momenta. One has[19]

$$p_i=\partial W(P_i,q^i)/\partial q^i \quad (9)$$

$$Q^i=\partial W(P_i,q^i)/\partial P_i, \quad (10)$$

where the Q^i are the new coordinates conjugate to P_i. When the (q^i, p_i) in H are expressed in terms of the (Q^i, P_i) using these equations, the new equations of motion become[20]

$$\dot{P}_i=-\partial H(P_i,Q^i)/\partial Q^i \quad (11)$$

$$\dot{Q}^i=\partial H(P_i,Q^i)/\partial P_i. \quad (12)$$

From (9) one finds

$$p_\Theta=(l^2-m_l^2\csc^2\Theta)^{1/2}, \qquad p_\Phi=m_l \quad (13a)$$

$$p_\theta=(j^2-m_j^2\csc^2\theta)^{1/2}, \qquad p_\phi=m_j. \quad (13b)$$

From (1) and (13), l, m_l, j, m_j are found to be the orbital angular momentum, its z component, the

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[14] In a collision $A+BC$,

$$\mu=m_A(m_B+m_C)/(m_A+m_B+m_C)$$

and

$$\mu_m=m_Bm_C/(m_B+m_C);$$

in a collision $A+BCD$,

$$\mu=m_AM/(m_A+M)$$

and

$$\mu_m r^2=[r_B^2m_B(M-m_B)^2+r_C^2m_C(M-m_C)^2+r_D^2m_D(M-m_D)^2]/M^2,$$

where $M=m_B+m_C+m_D$ and r_B, r_C, r_D are the distances of B, C, D from the center of mass of the rotor.

[15] Minor notational changes from Ref. 11 include interchange of R, Θ, Φ, Ψ and r, θ, ϕ, ψ and change of all β_i to $-\beta_i$. The present Eq. (5) is the same as Eq. (A-7) of the thesis and the present Eq. (29) is the same as that employed elsewhere in the thesis, as use of (31) shows.

[16] E.g., as in (a) D. Ter Haar, *Elements of Hamiltonian Mechanics* (North-Holland Publ. Co., Amsterdam, 1961), pp. 127–129; (b) p. 132 ff.; or (c) G. Birtwistle, *The Quantum Theory of the Atom* (Cambridge University Press, London, 1926), Chap. 19.

[17] The square root can either be positive or negative, and the customary procedure of letting it mean either is employed at this point.

[18] E.g., H. Goldstein, *Classical Mechanics* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1957), p. 244.

[19] Reference 18, p. 241, Eq. (8-11). Our W does not depend explicitly on time, so the $\partial F_2/\partial t$ there vanishes.

[20] Reference 18, p. 239, Eq. (8-5).

rotational angular momentum of the molecule and its z component, respectively.

The new momenta P_i are l, m_l, j, m_j and, when (8) is used, p_R. The coordinates Q^i conjugate to the latter are denoted below by Ψ, β_{m_l}, ψ, β_{m_j}, and R, respectively. From (9) and (10) one then finds

$$\bar{R}=\partial W/\partial\bar{p}_R=R, \tag{14}$$

$$\Psi=\partial W/\partial l=-\sin^{-1}[\csc i_l\cos\Theta], \tag{15}$$

$$\beta_{m_l}=\partial W/\partial m_l=\phi-\sin^{-1}[\cot i_l\cot\Theta], \tag{16}$$

$$\psi=\partial W/\partial j=-\sin^{-1}[\csc i_j\cos\theta], \tag{17}$$

$$\beta_{m_j}=\partial W/\partial m_j=\Phi-\sin^{-1}[\cot i_j\cot\theta], \tag{18}$$

where i_l is the angle between **l** and the z axis, and i_j is the angle between **j** and the z axis

$$\sin i_l=[1-(m_l/l)^2]^{1/2},\qquad \sin i_j=[1-(m_j/j)^2]^{1/2}. \tag{19}$$

Henceforth, the bar is omitted from the $\bar{p}_R$ and $\bar{R}$. Apart from a factor of 2π, the new variables j, m_j, l, m_l are actions, and the conjugate coordinates Ψ, β_{m_l}, ψ, β_{m_j} are angles.[16b] Similar remarks apply to j, k, and m in (37) and to P_v in (39).

One finds from (15) that Ψ is the angular position of **R** in the plane perpendicular to **l**, measured from the line of nodes (Fig. 1).[15] Similarly, from (17), ψ is the angular position of **r**, in the plane perpendicular to **j**, measured from the line of nodes. One also finds from (16) that $\beta_{m_l}+\pi/2$ is the azimuthal polar coordinate of **l** (Fig. 1), and from (18) $\beta_{m_j}+\pi/2$ is the azimuthal polar coordinate of **j**.

In terms of the Q^i and P_i, H becomes

$$H=(p_R^2/2\mu)+V(R,\gamma)+(l^2/2\mu R^2)+(j^2/2\mu_m r^2), \tag{20}$$

where

$$\cos\gamma=\cos\Theta\cos\theta+\sin\Theta\sin\theta\cos(\phi-\Phi) \tag{21}$$

and the angles Θ, θ, Φ, and ϕ are expressed in terms of the Q^i and P_i using relations readily derived from (15) to (19):

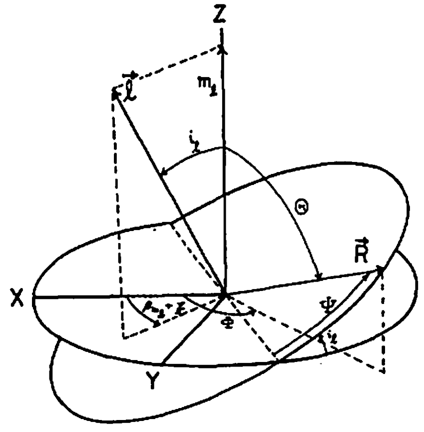

FIG. 1. The orientation of the instantaneous line-of-centers vector **R** is given by (Θ, Φ). The orientation of the instantaneous orbital angular momentum **l** is given by $(i_l, \beta_{m_l}+\pi/2)$. The position of **R** in the plane perpendicular to **l** is given by Ψ, an angle measured from the line of nodes.

$$\begin{aligned}\cos\Theta&=-[1-(m_l/l)^2]^{1/2}\sin\Psi,\\ \sin\Theta\cos\Phi&=-(m_l/l)\sin\Psi\sin\beta_{m_l}+\cos\Psi\cos\beta_{m_l},\\ \sin\Theta\sin\Phi&=(m_l/l)\sin\Psi\cos\beta_{m_l}+\cos\Psi\sin\beta_{m_l},\end{aligned} \tag{22}$$

$$\begin{aligned}\cos\theta&=[1-(m_j/j)^2]^{1/2}\sin\psi,\\ \sin\theta\cos\phi&=-(m_j/j)\sin\psi\sin\beta_{m_j}+\cos\psi\cos\beta_{m_j},\\ \sin\theta\sin\phi&=(m_j/j)\sin\psi\cos\beta_{m_j}+\cos\psi\sin\beta_{m_j}.\end{aligned} \tag{23}$$

Equations (11) and (12) provide the new exact equations of motion:

$$\begin{aligned}\dot{R}&=p_R\\ \dot{p}_R&=(l^2/\mu R^3)-\partial V/\partial R\end{aligned} \tag{24}$$

$$\begin{aligned}\dot{l}&=-\partial V_p/\partial\Psi\\ \dot{m}_l&=-\partial V_p/\partial\beta_{m_l}\\ \dot{\beta}_{m_l}&=\partial V_p/\partial m_l\\ \dot{\Psi}&=(l/\mu R^2)+\partial V_p/\partial l\end{aligned} \tag{25}$$

$$\begin{aligned}dj/dt&=-\partial V_p/\partial\psi\\ \dot{m}_j&=-\partial V_p/\partial\beta_{m_j}\\ \dot{\beta}_{m_j}&=\partial V_p/\partial m_j\\ \psi&=(j/\mu_m r^2)+\partial V_p/\partial j.\end{aligned} \tag{26}$$

These equations contain the variables R, p_R, l, $\cdots$, β_{m_j}, ψ. For some purposes, error estimates for example, it is more convenient for the new coordinates to contain Θ, Φ, R and the new momenta to contain j, m_j, and β_{m_j}, or for them to contain θ, ϕ, R and l, m_l, β_{m_l}, respectively. Such new sets of variables are immediately introduced by replacing the canonical transformation (8) by (27) or (28), respectively,

$$W=m_j\phi+\int(j^2-m_j^2\csc^2\theta)^{1/2}d\theta+\bar{P}_\Theta\Theta+\bar{P}_\Phi\Phi+\bar{P}_R R \tag{27}$$

$$W=m_l\Phi+\int(l^2-m_l^2\csc^2\Theta)^{1/2}d\Theta+\bar{P}_\theta\theta+\bar{P}_\phi\phi+\bar{P}_R(R). \tag{28}$$

The new variables and equations of motion are given in the Appendix. The latter are (24), (26), and (A1) in the first case and (24), (25), and (A2) in the second.

An approximate solution of the equations of motion is obtained by replacing the Q^i and P_i by their elastic collision values $\bar{Q}^i$, $\bar{P}_i$ in the right-hand sides of these equations. Thereby, for $P_i=l$, m_l, j, m_j and $Q^i=\beta_{m_l}$ and β_{m_j} we have, regardless of whether W is chosen to be (8), (27), or (28),

$$\Delta P_i \cong -\int_{-\infty}^{\infty} \partial V_p(\tilde{R}, \bar{\gamma})/\partial \tilde{Q}^i dt$$

$$\Delta Q^i = \int_{-\infty}^{\infty} \partial V_p(\tilde{R}, \bar{\gamma})/\partial \bar{P}_i dt. \qquad (29)$$

An estimate of the error in (29) is obtained by expanding the partial derivatives in (29) in powers of $Q^i - \tilde{Q}^i$ and $P_i - \bar{P}_i$ and retaining the first power. Thus, for example,

$$(\Delta P_i)_{\mathrm{exact}} \cong \Delta P_i + \int_{-\infty}^{\infty} \sum_{j=1}^{N} \left(\frac{\partial^2 V_p}{\partial Q^j \partial Q^i} (Q^j - \tilde{Q}^j) + \frac{\partial^2 V_p}{\partial P_j \partial Q^i} (P_j - \bar{P}_j) \right) dt$$

$$(\Delta Q^i)_{\mathrm{exact}} \cong \Delta Q^i + \int_{-\infty}^{+\infty} \sum_{j=1}^{N} \left[\left(\frac{\partial^2 V_p}{\partial Q^j \partial P_i} \right) (Q^j - \tilde{Q}^j) + \left(\frac{\partial^2 V_p}{\partial P_j \partial P_i} \right) (P_j - \bar{P}_j) \right] dt, \qquad (30)$$

where the derivatives are evaluated at $Q^k = \tilde{Q}^k$, $P_k = \bar{P}_k$.

When $V_p(R, \gamma)$ is a sum of terms of the form $a_n V_n(R) P_n(\cos\gamma)$, P_n being a Legendre polynomial, and then expressed in terms of the Q^i and P_i one obtains sums of terms such as $V_n(R)(g_1 \sin\tilde{\Psi} \sin\tilde{\psi} + g_2 \sin\tilde{\Psi} \cos\tilde{\psi} + g_3 \cos\tilde{\Psi} \sin\tilde{\psi} + g_4 \cos\tilde{\Psi} \cos\tilde{\psi})^m$, where $m \leq n$. Here, the g_i are functions of the initial values of the constants of the motion. Thus, from (29), Δl, Δm_l, $\Delta\beta_{m_l}$, Δj, Δm_j, and $\Delta\beta_{m_j}$ are approximately equal to integrals of the $V_n(r)$ times oscillating factors. The initial orientations of the particles only appear outside these integrals.

The properties of the elastic collision are needed for use of (29) and (30). They are obtained from (24) to (27) by setting $V_p = 0$ on the right-hand sides of these equations. Integration then yields

$$\int \left[\tfrac{1}{2}\mu \left(E - \frac{l^2}{2\mu \tilde{R}^2} - \frac{j^2}{2\mu_m r^2} - V_0(\tilde{R}) \right) \right]^{-1/2} d\tilde{R} = t - \beta_E,$$

$$\tilde{\Psi} = \int_0^t [l/\mu \tilde{R}^2(t)] dt - \beta_l,$$

$$\tilde{\psi} = \omega t - \beta_j, \qquad (31)$$

where ω denotes $j/\mu_m r^2$; β_E, β_l, and β_j are phases describing the positions of $\mathbf{r}$ and $\mathbf{R}$ at $t = 0$.[21] Equations (24)–(27) also illustrate clearly that l, m_l, β_{m_l}, j, m_j, and β_{m_j} for an elastic collision are constants, and so equal their initial values.

The first integral in (31) can be expressed in terms of elliptic integrals when $V_0(R)$ is of a suitable form, e.g., when it varies as r^{-6}, r^{-4}, etc.[22] Otherwise, the integral is evaluated numerically.

In applications in Part II, we have found it convenient to obtain (29) from any of the three sets of equations of motion mentioned earlier but to obtain the error estimates in (30) using (24), (26), (A1) or (24), (25), (A2). Also, in Eq. (1) and all other equations but (21) the coordinate axes which define Θ, Φ (and i_l, β_{m_l}) need not have the same orientation as those which define θ, ϕ (and i_j, β_{m_j}); the kinetic-energy contributions of μ and μ_m in (1) are individually rotationally invariant. In applications in Part II of (24)–(26) or of any of the other equations it has been convenient to choose two sets of axes simultaneously, one in which the $\tilde{\mathbf{R}}$ motion is simply described and the other in which the $\tilde{\mathbf{r}}$ one is. Equation (21) for $\cos\gamma$ is replaced by the appropriate equation.

GENERAL COLLISIONS

The Hamilton–Jacobi formalism in the preceding section is readily extended to rotational–vibrational–translational energy transfer involving more complex systems. The Hamiltonian H is

$$H = (2\mu)^{-1} \{ p_R^2 + (1/R^2) [p_\Theta^2 + (p_\Phi^2 / \sin^2\Theta)] \} + H_A + H_B + V(R, \gamma_k, q_A^v, q_B^v), \qquad (32)$$

where H_A and H_B denote the rotational–vibrational Hamiltonian for the colliding particles A and B, respectively; the γ_k's are the angles describing the relative orientation of A and B; the q_A^v's and q_B^v's are the vibrational coordinates of A and B, respectively, and the remaining symbols retain their previous significance. H_A is a function only of q_A^i and p_{iA}, the rotational–vibrational coordinates and conjugate momenta of A. Analogous remarks apply to H_B.

Solution of the Hamilton–Jacobi for the elastic collision, in which V is replaced by a suitably averaged value $V_0(R)$, yields the generating function $W(\alpha_i, q^i)$

$$W(\alpha_i, q^i) = m_l \Phi + \int (l^2 - m_l^2 \csc^2\Theta)^{1/2} d\Theta + W_A + W_B + W_R, \qquad (33)$$

where W_A and W_B are the generating functions arising from H_A and H_B, respectively. W_R is the generalization of (7)

$$W_R = \int \{ 2\mu [E - (l^2/2\mu R^2) - E_A - E_B - V_0] \}^{1/2} dR, \qquad (34)$$

where E_A and E_B are the rotational–vibrational energies of A and B, expressed in terms of action variables.

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[21] Another significance of $\beta_E - t$, is that it is the coordinate conjugate to the "momentum" E, when the generating function $W - Et$ is used, where W is given by (5) (e.g., compare Ref. 11, taking the present Ref. 15 into account).

[22] Reference 18, pp. 73–76.

For example, if A is an atom and B is a linear rigid rotor, E_A and W_A are absent, E_B is the $j^2/2\mu_m r^2$ term in (7), and W_B is the sum of the second and fourth terms in (6).

A second useful generating function is the counterpart of (8)

$$W = m_l\Phi + \int (l^2 - m_l^2 \csc^2\Theta)^{1/2} d\Theta + W_A + W_B + \bar{p}_R R. \tag{35}$$

In either case, Eqs. (9) to (13a) again prevail. With W given by (35), the other equations of the preceding section which remain applicable are those involving only R, Θ, Φ, i.e., Eqs. (14)–(16) and (24)–(25). The analog of (29) can also be written, with $\bar{\gamma}$ replaced by $\bar{\gamma}_k$, $\bar{q}_A{}^v$, $\bar{q}_B{}^v$ and with the P_i denoting l, m_l, and the action variables appropriate to H_A and H_B. (In the preceding section the latter were j and m_l.)

For example, when B is a rigid symmetric-top molecule we have[23]

$$H_B = (1/2I_x)[p_\theta^2 + (p_\phi - p_\chi \cos\theta)^2 \csc^2\theta] + (p_\chi^2/2I_z), \tag{36}$$

where θ, ϕ, and χ are the Euler angles describing the orientation of B, and $I_x(=I_y)$ and I_z are its principal moments of inertia.

We then have[24]

$$W_B = m\phi + k\chi + \int [j^2 - k^2 - (m - k\cos\theta)^2 \csc^2\theta]^{1/2} d\theta, \tag{37}$$

where the constants m, k, and j arise during the separation of variables. From (9), (35), and (37) one finds

$$p_\theta = \int [j^2 - k^2 - (m - k\cos\theta)^2 \csc^2\theta]^{1/2} d\theta$$

$$p_\phi = m, \qquad p_\chi = k. \tag{38}$$

From (36) and (37) the separation constants j, k, and m are found to equal molecule B's total rotational angular momentum, **j**, the component of **j** along the figure axis of B, and its component along the space-fixed z axis. The integral in (37) can be expressed in terms of a standard one on introducing a new variable $u = mk - j^2\cos\theta$. The variables conjugate to j, k, and m are found from (10) and (37); (11) and (12) yield the new equations of motion.

When the assumption of a rigid molecule in the preceding section is removed, the generating function (6) contains an additional term, W_v. For example, when the vibrational motion of the diatomic molecule is harmonic and when the new variables for the oscillator Q^v and P_v are chosen to be angle-action variables, W_v is found from the solution of the Hamilton–Jacobi equation to be[25]

$$W_v(q^v, v) = (P_v/2\pi)(u + \tfrac{1}{2}\sin 2u), \tag{39}$$

where

$$u = \sin^{-1}(\mu\omega\pi/P_v)^{1/2} q^v, \tag{40}$$

and where $\omega/2\pi$ is the vibrational frequency. The vibrational energy equals $P_v\omega/2\pi$, and the new equations are again given by (11) and (12). Similarly, W_A and W_B in (35) contain a term (39) for each normal mode in A and B.

Once again, in the case of general collisions, it is sometimes convenient to replace (33) by the analog of (27) or (28).

CONCLUDING REMARKS

The Hamilton–Jacobi formalism provides a generating function which can be used to transform the equations of motion into a convenient form. An approximate version, given by (29), utilizes as the unperturbed problem the elastic collision and, hence, the behavior of the internal motions at infinite separation. A similar zeroth-order approximation is commonly employed in quantum-mechanical treatments.[26]

Comparison of the approximate and exact classical results is given in Part II for rotational–translational energy transfer between an atom and a rigid linear molecule. The comparison reveals that when the "distortion" of the internal motion is small, in the sense of a high enough ratio of rotational to orbital moment of inertia or high enough rotational frequency, the cited approximation is a reasonable one at least for cases examined thus far. Small distortion as defined above does not necessarily imply small fractional change in rotational energy. Analogous remarks may be expected to apply to quantum-mechanical treatments.

A similar situation exists for the vibrational–translational energy transfer between an atom A and a

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[23] E.g., M. Born, *The Mechanics of the Atom* (Frederick Ungas Publ. Co., New York, 1960), p. 27. We employ the Euler angle defined in E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., New York, 1955), p. 285.

[24] E.g., compare A. G. Webster, *Dynamics of Particles* (B. Gr. Teubner, Leipzig, 1904), p. 297 ff.

[25] E.g., H. C. Corben and P. Stehle, *Classical Mechanics* (John Wiley & Sons, Inc., 1960), p. 190. For some purposes, vibrational variables related to, but different from, angle-action ones may be still more convenient. [Compare discussion of an equation (90) in R. A. Marcus, J. Chem. Phys. **49**, 2610 (1968).]

[26] The latter often contain additional approximations, such as one which results in expressing the transition probability in terms of an integral involving only initial and final unperturbed wavefunctions rather than allowing for intermediate ones as well. Contrast, for example, Eq. (7.26), p. 48, or (1.17), p. 114, of G. Ludwig, *Die Grundlagen der Quantenmechanik* (Springer–Verlag, Berlin, 1954) [or the expression for P_{mn} in E. Kerner, Can. J. Phys. **36**, 371 (1958), p. 373] with the more usual (first-order) expressions for the forced linear-oscillator problem. Compare C. E. Treanor, J. Chem. Phys. **43**, 532 (1965).

molecule *BC* on a line, when small "distortion" is interpreted as a high enough mass-ratio involving m_B.[27]

APPENDIX: VARIABLES AND EQUATIONS OF MOTION ARISING FROM EQ. (27) OR (28)

The new momenta in (27) are $\bar{p}_R$, $\bar{p}_\Theta$, $\bar{p}_\Phi$, j, and m_j. Use of Eqs. (10) and (27) shows that the new coordinates are R, Θ, Φ, the ψ given by (17) and the β_{m_j} given by (18). (We henceforth drop all bars over $\bar{\bar{R}}$, $\bar{\bar{\Theta}}$, and $\bar{\bar{\Phi}}$, therefore.) Equation (9) then yields (13b), while (17) and (18) yield (23). Equations (11), (12), and (28) yield (24), (26), and (A1) as new equations of motion

$$\dot{p}_\Theta = -\partial V_p/\partial\Theta, \qquad \dot{p}_\Phi = -\partial V_p/\partial\Phi$$
$$\dot{\Theta} = p_\Theta/2\mu R^2, \qquad \dot{\Phi} = p_\Phi/2\mu R^2 \sin^2\Theta. \qquad \text{(A1)}$$

The new momenta in (28) are $\bar{p}_R$, $\bar{p}_\theta$, $\bar{p}_\phi$, l, and m_l. Use of (10) and (28) yields R, θ, ϕ, the Ψ given by (15), and the β_{m_l} given by (16) as the new coordinates. (Thus, again all bars are omitted.) Equation (9) yields (13a), while (15) and (16) yield (22). Equations (11), (12), and (28) yield (24), (25), and (A2) as the new equations of motion

$$\dot{p}_\theta = -\partial V_p/\partial\theta, \qquad \dot{p}_\phi = -\partial V_p/\partial\phi$$
$$\dot{\theta} = p_\theta/2\mu_m r^2, \qquad \dot{\phi} = p_\phi/2\mu_m r^2 \sin^2\theta. \qquad \text{(A2)}$$

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[27] This mass ratio is $m_B(m_A+m_B+m_C)/m_A m_C$ introduced by J. D. Kelley and M. Wolfsberg, J. Chem. Phys. **44**, 324 (1966). Compare M. Attermeyer, Ph.D. thesis, University of Illinois, December 1968.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 10 15 NOVEMBER 1968

Measurement and Analysis of Mössbauer Data for Compounds Containing ^{125}Te

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(Received 26 January 1968)

Mössbauer isomer shifts and quadrupole splittings are reported for a number of tellurium compounds. The isomer-shift data are analyzed by setting up localized orbitals and converting to their equivalent delocalized orbitals in order to calculate the electron density at the ^{125}Te nucleus. Similarities between data for tellurium and tin compounds are noted. The theoretical calculations confirm the expectation that hydrogenic orbitals are more appropriate for calculations of electron density at a nucleus than the Slater-type orbitals generally used in molecular-orbital calculations.

I. INTRODUCTION

Although some data[1–8] have been reported for the Mössbauer effect using ^{125}Te as the nuclear probe, more data needed to be obtained before the results could be subjected to a theoretical analysis. This paper reports data for isomer shifts and quadrupole splittings on 12 previously unreported compounds, and presents a theoretical treatment of the known Mössbauer isomer shifts of tellurium. This treatment is an extension of the quantum-mechanical approach which was employed previously in our laboratory for ^{31}P NMR chemical shifts,[9] which has recently been extended and compared with molecular SCF calculations,[10] and which was used in an analysis of ^{119}Sn Mössbauer data.

II. EXPERIMENTAL DETAILS

A. Instrumentation

The instrument used in this study was built around the model AM-1 constant-acceleration Mössbauer spectrometer produced by the Nuclear Science and Engineering Corporation. The complimentary equipment included a model 34-12B multichannel analyzer made by Radiation Instruments Development Laboratory. Useful readout of the accumulated data was accomplished by using a Hewlett–Packard 562A digital recorder and/or an RIDL 99-24A Punch/Type

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