

## Separation of the Energy of Overall Rotation in Any $N$ -Body System

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A general exact procedure for separation of the energy of the overall rotation from the "internal" (vibrational) energy in any (arbitrarily floppy)  $N$ -body system is formulated. It is based on following the detailed dynamics of the system and it retains all the dynamical couplings allowing for the flow of energy between the rotation and vibrations. Still, it leads to a complete instantaneous separation of the energies in that the Coriolis term in the Hamiltonian is zero at all times. The utility of the new scheme is illustrated.

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The general problem of separation and characterization of the overall rotation in any (not necessarily rigid or near rigid)  $N$ -body system is among the few still unsolved problems of traditional classical mechanics. While an elegant description of the at times, indeed, complex force-free motion of a rigid body about a fixed point has been given more than a century ago,<sup>1</sup> the description of rotational motion of highly nonrigid systems remains a challenge. The remedy for the case of floppy systems is usually formulated in terms of near-rigid (or "semirigid") bodies in which the rotational motion is executed in conjunction with (small-amplitude) oscillations. The validity of the near-rigid model is based on a Born-Oppenheimer-type time-scale argument and separability, in the case of molecules, of the rotational, vibrational, and electronic degrees of freedom. The field of theoretical rovibrational spectroscopy is essentially the quantum-mechanical (or semiclassical) version of this model: The rotational energy spectrum is calculated as that of a spherical, symmetric or asymmetric top (rigid or semirigid). The extension to semirigid molecules usually heavily exploits their symmetry properties. None of the approaches is, however, general enough to deal with the case of an arbitrarily floppy, nonsymmetric, rotating (nonzero total angular momentum) molecule. The need in a more comprehensive approach to characterization of the rotational motion arises not only in spectroscopy. Classical dynamical studies of phase properties (e.g., solidlike versus liquidlike) and isomerization transitions in  $N$ -body systems, such as atomic clusters, revealed the extremely important and quite intricate role of the total angular momentum on the detailed time evolution of these systems.<sup>2,3</sup> To fully understand the mechanism through which the overall rotation impacts on the phase change and isomerization dynamics one must be able to isolate this rotation in any  $N$ -atom system; and this is while by virtue of the phenomenon at hand no *a priori* restriction on the degree of nonrigidity of the system may or should be imposed.

In this Letter we formulate a general prescription for separation of the energy of the overall rotation from that

of the "internal" (vibrational) motion in any isolated  $N$ -body system without imposing any restriction on the degree of its floppiness or making any assumption regarding its symmetry. Because of our original interest lying in dynamics we consider the  $N$ -body system as a classical dynamical object evolving in time in accordance with Hamilton equations of motion under forces defined by a known potential  $V(\{\mathbf{r}_i\})$ ,  $i=1, \dots, N$ . To eliminate the translational motion we refer the coordinates  $\{\mathbf{r}_i\}$  and the momenta  $\{\mathbf{p}_i\}$  of the constituent particles to the center-of-mass laboratory-oriented system of coordinates. Our procedure capitalizes on the known classical dynamical relations for a rotating true rigid body. Recall<sup>4</sup> that a force-free rotation of a true rigid body about a fixed point (e.g., its center of mass) is fully characterized by the time evolution of its angular velocity  $\boldsymbol{\omega}^{\text{rb}}(t)$ . This evolution is most conveniently described by Euler equations formulated in the body-fixed principal-axes system of coordinates; an analytical solution exists in terms of elliptic functions. Although  $\boldsymbol{\omega}^{\text{rb}}(t)$  changes with time, the rigid-body total angular momentum in the laboratory-oriented frame,

$$\mathbf{L}^{\text{rb}} = \mathbf{I}^{\text{rb}}(t) \cdot \boldsymbol{\omega}^{\text{rb}}(t), \quad (1)$$

and its energy,

$$E^{\text{rb}} = \frac{1}{2} \boldsymbol{\omega}^{\text{rb}}(t) \cdot \mathbf{L}^{\text{rb}}, \quad (2)$$

are constants of motion.  $\mathbf{I}^{\text{rb}}(t)$  in Eq. (1) is the instantaneous tensor of inertia of the rigid body in the laboratory-oriented system of coordinates. If the rigid body consists of  $N$ -point particles of masses  $m_i$  ( $i=1, \dots, N$ ) then  $\mathbf{I}^{\text{rb}}(t)$  can be expressed through the coordinates  $\mathbf{r}_i(x_i, y_i, z_i)$  of these particles as a  $3 \times 3$  matrix with matrix elements

$$I_{aa}(t) = \sum_i m_i [r_i^2(t) - \alpha_i^2(t)], \quad (3)$$

$$I_{a\beta}(t) = - \sum_i m_i \alpha_i(t) \beta_i(t); \quad a, \beta (\neq a) = x, y, z.$$

Consider now a nonrigid  $N$ -particle system. Integrat-

ing numerically its Hamilton equations in coordinates  $\mathbf{r}_i(t)[x_i(t), y_i(t), z_i(t)]$ , we can calculate its instantaneous tensor of inertia  $\mathbf{I}(t)$  by substituting these coordinates into Eqs. (3). Even though one may find that  $\mathbf{I}(t_0) = \mathbf{I}^{\text{rb}}(t_0)$  for a certain true rigid body at a certain  $t = t_0$ , the equality will not, in general, remain valid at  $t > t_0$ . For so defined  $\mathbf{I}(t)$  and total angular momentum  $\mathbf{L}$  of the system,

$$\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i, \quad (4)$$

which is a constant of motion, we can introduce a vector  $\boldsymbol{\omega}_L^{\text{rb}}(t)$  satisfying the equation

$$\mathbf{L} = \mathbf{I}(t) \cdot \boldsymbol{\omega}_L^{\text{rb}}(t). \quad (5)$$

The meaning of  $\boldsymbol{\omega}_L^{\text{rb}}(t)$ , which is defined by Eq. (5) uniquely,<sup>5</sup> is easily understood: It is the angular velocity with which the nonrigid system of total angular momentum  $\mathbf{L}$  and tensor of inertia  $\mathbf{I}(t)$  would rotate if at instant  $t$  it were a true rigid body. Or in other words, at any time  $t$  we can associate with the nonrigid system a rigid body rotating with angular velocity  $\boldsymbol{\omega}_L^{\text{rb}}(t)$  and having the same  $\mathbf{L}$  and  $\mathbf{I}(t)$  as the nonrigid system; the motion of this rigid body represents the instantaneous overall rotation of the nonrigid system. Thus by assigning  $\boldsymbol{\omega}_L^{\text{rb}}(t)$  to a nonrigid system we separate out its overall or "rigid-body" part rotation. The energy of this rotation is

$$E_L^{\text{rb}}(t) = \frac{1}{2} \boldsymbol{\omega}_L^{\text{rb}}(t) \cdot \mathbf{L}. \quad (6)$$

Since the time evolution of  $\mathbf{I}(t)$  is ultimately defined by Hamilton equations (and not by those for a true rigid body) the time evolution of  $\boldsymbol{\omega}_L^{\text{rb}}(t)$ , defined by Eq. (5), is also different from that for a true rigid body. This means that a different rigid body corresponds to our nonrigid system at different times. A consequence of this is that  $E_L^{\text{rb}}(t) \neq \text{const}$  in distinct dissimilarity with the case of a true rigid body. Alternatively, one can picture the time evolution of the overall rotation of a nonrigid system as represented by a rotational motion of a changing rigid body. Although the notion of a changing rigid body may appear as inherently contradictory it correctly captures the essence of the effect. The continuous change in the rigid body is essentially the continuous change in the instantaneous ellipsoid of inertia corresponding to the nonrigid system. The term rigid body is retained to emphasize that at any instant  $t$  the motion of this phantom changing body is fully described by a single vector  $\boldsymbol{\omega}_L^{\text{rb}}(t)$ .

Using  $E_L^{\text{rb}}$  [Eq. (6)] we can write the total kinetic energy of any nonrigid system as a sum of the energy of its overall rotation and the "rest," to be called internal (vibrational) energy  $E^{\text{int}}$ :

$$\sum_i \frac{\mathbf{p}_i^2(t)}{2m_i} = E_L^{\text{rb}}(t) + E^{\text{int}}(t). \quad (7)$$

That such a partitioning can be made always is guaranteed by the following.

*Theorem:* Of all the compositionally identical  $N$ -particle systems with the same configuration and total angular momentum  $\mathbf{L}$  in the center-of-mass laboratory-oriented system of coordinates, the (instantaneous) rigid body has the lowest total kinetic energy.

*Proof:* Let the set  $\{\mathbf{r}_i\}$  define the configuration of the systems and  $\{\mathbf{p}_i^{\text{rb}}\}$  and  $\{\mathbf{p}_i\}$  be the momenta of the particles comprising the rigid body and the arbitrary other (nonrigid) system, respectively. Defining  $\Delta\mathbf{p}_i = \mathbf{p}_i - \mathbf{p}_i^{\text{rb}}$ , we can write

$$\mathbf{L} = \sum_i \mathbf{r}_i \times \mathbf{p}_i = \sum_i \mathbf{r}_i \times \mathbf{p}_i^{\text{rb}} + \sum_i \mathbf{r}_i \times \Delta\mathbf{p}_i.$$

Since  $\sum_i \mathbf{r}_i \times \mathbf{p}_i^{\text{rb}} = \mathbf{L}$ ,

$$\sum_i \mathbf{r}_i \times \Delta\mathbf{p}_i = 0. \quad (8)$$

The total kinetic energy of the nonrigid system is

$$\sum_i \frac{\mathbf{p}_i^2}{2m_i} = \sum_i \frac{(\mathbf{p}_i^{\text{rb}})^2}{2m_i} + \sum_i \frac{(\Delta\mathbf{p}_i)^2}{2m_i} + \sum_i \frac{\mathbf{p}_i^{\text{rb}} \cdot \Delta\mathbf{p}_i}{m_i}.$$

Since  $\mathbf{p}_i^{\text{rb}} = m_i(\boldsymbol{\omega}_L^{\text{rb}} \times \mathbf{r}_i)$  the last sum, which will be recognized as the Coriolis term,

$$\begin{aligned} \sum_i \frac{\mathbf{p}_i^{\text{rb}} \cdot \Delta\mathbf{p}_i}{m_i} &= \sum_i (\boldsymbol{\omega}_L^{\text{rb}} \times \mathbf{r}_i) \cdot \Delta\mathbf{p}_i \\ &= \boldsymbol{\omega}_L^{\text{rb}} \cdot \sum_i \mathbf{r}_i \times \Delta\mathbf{p}_i = 0, \end{aligned}$$

in view of Eq. (8). Thus

$$\begin{aligned} \sum_i \frac{\mathbf{p}_i^2}{2m_i} &= \sum_i \frac{m_i}{2} (\boldsymbol{\omega}_L^{\text{rb}} \times \mathbf{r}_i) (\boldsymbol{\omega}_L^{\text{rb}} \times \mathbf{r}_i) + \sum_i \frac{(\Delta\mathbf{p}_i)^2}{2m_i} \\ &= E_L^{\text{rb}} + \sum_i \frac{(\Delta\mathbf{p}_i)^2}{2m_i}. \end{aligned} \quad (9)$$

From here the statement of the theorem is obvious. A few remarks are in order. First, it follows immediately that  $E^{\text{int}} = \sum_i (\Delta\mathbf{p}_i)^2 / 2m_i$ , where  $\Delta\mathbf{p}_i = \mathbf{p}_i - m_i(\boldsymbol{\omega}_L^{\text{rb}} \times \mathbf{r}_i)$ . We can then introduce an internal temperature  $T$  defined as  $2\bar{E}^{\text{int}} / (3N - 6)k$ , where  $\bar{E}^{\text{int}}$  is the appropriate (ensemble or time) average of  $E^{\text{int}}$  and  $k$  is the Boltzmann constant. Second, as seen from Eq. (9), the scheme presented accomplishes a complete instantaneous separation of the energy of overall rotation in any nonrigid system from the internal (vibrational) energy in that the Coriolis term is zero at all times. This is a consequence of the fact that in this scheme the vibrations do not contribute to the total angular momentum at all [Eq. (8)]. Note that the complete instantaneous separation (apportionment) of the energies is achieved despite the fact that the dynamical coupling in the system is fully retained and the rotation and vibrations exchange energy. Third, looking upon  $\Delta\mathbf{p}_i$  in Eq. (9) as a rate of displacement in the center-of-mass system of coordinates, which moves with the velocity  $\boldsymbol{\omega}_L^{\text{rb}}(t)$  with

respect to the laboratory-oriented system, one essentially introduces an Eckart-type rotating frame<sup>6</sup> which satisfies a generalized Eckart-type condition, Eq. (8). [The Eckart condition for the near-rigid limit is recovered by the integration of Eq. (8) in which the  $\mathbf{r}_i(t)$ 's are substituted by constants  $\mathbf{r}_{0i}$ 's.]

Since  $\mathbf{I}(t) = \mathbf{I}(\{\mathbf{r}_i(t)\})$ , also  $\boldsymbol{\omega}_L^{\text{rb}}(t) = \boldsymbol{\omega}_L^{\text{rb}}(\{\mathbf{r}_i(t)\})$  [Eq. (5)] and  $E_L^{\text{rb}}(t) = E_L^{\text{rb}}(\{\mathbf{r}_i(t)\})$  [Eq. (6)]. Introducing an effective potential

$$V_L(\{\mathbf{r}_i\}) = E_L^{\text{rb}}(\{\mathbf{r}_i\}) + V(\{\mathbf{r}_i\}) \quad (10)$$

and taking into account Eq. (9) [or Eq. (7)] we obtain

$$\begin{aligned} H &= \sum_i \frac{\Delta \mathbf{p}_i^2}{2m_i} + V_L(\{\mathbf{r}_i\}) \\ &= E^{\text{int}}(\{\Delta \mathbf{p}_i\}) + V_L(\{\mathbf{r}_i\}). \end{aligned} \quad (11)$$

$V_L(\{\mathbf{r}_i\})$  can be referred to as the rovibrational potential surface. The internal motion of a rotating nonrigid system is effectively driven by this surface.<sup>7</sup> A continuous path on it describes the continuous adjustment of the system in terms of  $\boldsymbol{\omega}_L^{\text{rb}}(\{\mathbf{r}_i\})$  and  $E_L^{\text{rb}}(\{\mathbf{r}_i\})$  to its changing configuration [i.e., changing  $\mathbf{I}(\{\mathbf{r}_i\})$ ] to keep  $L$  constant. Equation (11) suggests a new quenching procedure: By removing  $E^{\text{int}}$  from the system one freezes out its vibrations, preserving its  $L$ ; i.e., preserving its overall rotation. The minima of  $V_L(\{\mathbf{r}_i\})$  correspond to equilibrium structures of the rotating  $N$ -particle system. These structures are attained when the net force acting on every individual particle plays only the role of the corresponding centripetal force.

To illustrate the utility of the concepts and techniques described above we present a few examples of their application in isoergic dynamical studies of small clusters. Figure 1 displays short-time (5 psec) averages of different kinetic energies per particle as functions of time in a rotating and nonrotating  $\text{Ar}_{13}$  cluster (for computational details see Refs. 3 and 8). The pronounced difference in patterns of the total kinetic energy [Fig. 1(a)] can be understood qualitatively by taking into account the differences in the topologies of  $V(\{\mathbf{r}_i\})$  and of  $V_L(\{\mathbf{r}_i\})$ . That these topologies are indeed different follows from the fact that  $E_L^{\text{rb}}(\{\mathbf{r}_i\}) \neq \text{const.}$  The rotation confines the cluster to distinct parts of configuration space with lower potential (higher kinetic) energy as compared to the case of no rotation. Each one of these parts is capable of trapping the cluster for an appreciable time and corresponds to a different rotating isomer; the isomers were identified through quenching of the internal energy. The appropriate counterpart for the kinetic energy of the nonrotating cluster is the internal energy of the rotating cluster. In Fig. 1(b) the decomposition of the total kinetic energy into the energy of the overall rotation (rigid body) and the internal (vibrational) energy is shown. A point to note is that although the total kinetic energy of the rotating cluster is higher, it is internally colder than the nonrotating cluster. The graphs

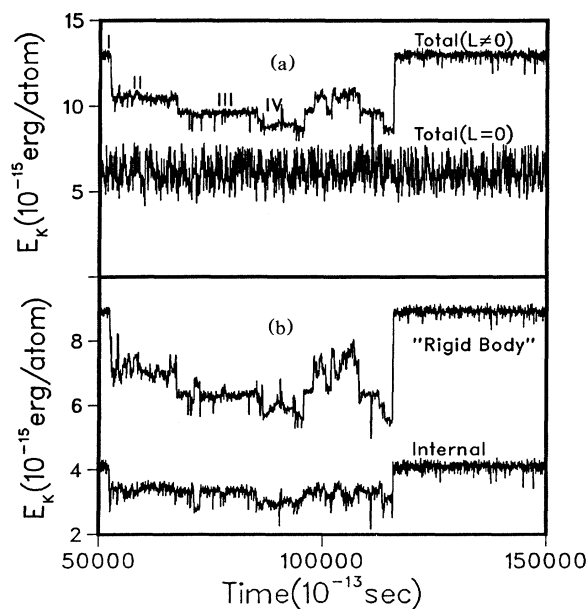


FIG. 1. Short-time (5 psec) averaged kinetic energies per atom as functions of time. Total energy  $E_{\text{tot}} = -0.379 \times 10^{-13}$  erg/atom. (a) Total kinetic energies for  $L=0$  and  $4.29 \times 10^{-25}$  erg·sec. (b) Energy of overall rotation ("rigid body") and internal energy for  $L = 4.29 \times 10^{-25}$  erg·sec. Roman numerals denote different isomers.

clearly indicate that changes in the rigid body (overall rotation) accompany isomerization transitions. These transitions may (such as for isomers I and II or III and IV) or may not (such as for isomers II and III) be accompanied by changes in the internal energy (internal temperature; here the temperature is referred to the internal energies averaged over single isomers). That the separation of the energies of the overall rotation and vibrations is indeed complete is illustrated in Fig. 2 which displays typical pictures generated by the internal energy quenching procedure. As the internal energy is extracted the evolving nonrigid system and corresponding changing rigid body consolidate into a rotating apparently rigid (nonvibrating) body with an asymptotically constant  $E^{\text{rb}}$  [Fig. 2(a)]. That the result of the quenching is indeed a rotating apparently rigid body is corroborated also by Fig. 2(b). The erratic changes in the angle  $\theta$  between the  $\boldsymbol{\omega}^{\text{rb}}$  and the space-fixed vector  $L$ , reflecting the nonrigid character of the cluster before quenching, evolve, as a result of quenching, into a regular pattern corresponding to the characteristic Poincot nutation<sup>1,4</sup> for a true rigid body.

Summarizing, we have presented an exact (no approximations) general procedure for separation of the energy of the overall rotation from that of the vibrational motion in any  $N$ -body system irrespective of the degree of its nonrigidity. The procedure is based on following the exact time evolution of the system and it retains all

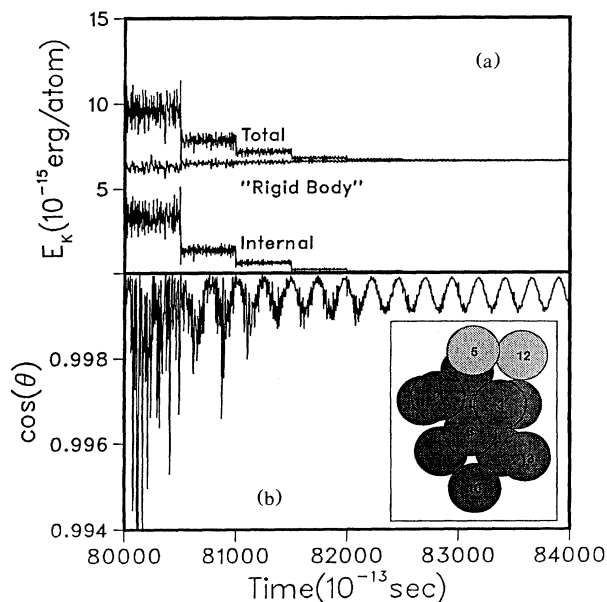


FIG. 2. Internal energy quenching history for isomer III (each point is an average over 0.25 psec); quenching has been performed every 50 psec. (a) Kinetic energies per particle. (b) Corresponding evolution of the angle  $\theta$  between  $\omega^{\text{rb}}$  and  $L = \text{const}$ . Inset: The structure of the quenched rotating cluster; its potential energy is  $V = -0.663 \times 10^{-12}$  erg.

the dynamical couplings; still it results in a *complete* instantaneous decoupling of the energy of overall rotation from those of vibrations giving zero Coriolis contribution in the Hamiltonian. The distinction of the new procedure from the earlier ones, which also explains why the

latter could achieve only an approximate or incomplete separation of the energies, is that it accomplishes the separation of the *energies*, circumventing the problem of separation of the *coordinates*. It effectively defines a rotating frame which can be viewed as an Eckart-type frame satisfying a generalized Eckart-type condition; this condition is the requirement that the total vibrational angular momentum is zero. The scheme already proved its power in our dynamical studies<sup>3</sup> of small clusters to be reported in more detail separately.<sup>7</sup> We suggest its semiclassical or quantal extensions (yet to be formulated) may open a new avenue to the rovibrational spectroscopy of highly nonrigid and/or highly energized species.

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