

Center-of-mass motion of an N -particle atom or ion and the Thomas-Reiche-Kuhn sum rule

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The Thomas-Reiche-Kuhn sum rule is corrected for the motion of the atomic center of mass, and generalized to include ions. The results are specialized to the case of a two-level atom or ion.

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Sum rules are often used to evaluate integral properties of response functions, for systems governed by a Hamiltonian H in the presence of some interaction; in particular, they enable integrated cross sections to be determined without the need to solve the eigenvalue equation [1]. The Thomas-Reiche-Kuhn (TRK) sum rule was one of the first such rules to be found, and relates the atomic matrix elements of an electric-dipole interaction with the corresponding eigenenergies. It is now a part of the history of quantum mechanics that the existence of the TRK sum rule led Heisenberg to believe that the canonical commutator between the conjugate variables of position and momentum must be valid [2] – the sum rule had originally been proved before the advent of wave mechanics [3].

But what if the commutator between the atomic dynamical variables is not canonical? This situation arises, for example, in the case where an atom is modeled in terms of a finite number of eigenstates, such as a two-level system. Here, the TRK sum rules must be modified to take account of the noncanonical nature of the fundamental commutator [4]; a fact which resolves an apparent paradox involving the usual form of the TRK sum rule and a two-level atom. A similar situation occurs when an atom is considered to possess an overall gross motion, characterized by the dynamics of its center of mass \mathbf{R} . In such a case, it will be seen below that the commutator between the internal atomic dynamical variables is also noncanonical.

This report accounts for the effects of gross motion in the TRK sum rule, and, with a generalization to N -particle atoms, extends the rule to include the case of ions. The general theory, as is to be expected, has some formal similarities with the well-known derivation of the nuclear electric-dipole sum rule [1]. The theory will be specialized to atoms and ions comprising a finite number of equally spaced eigenenergies. Such an investigation is timely in view of theoretical developments in the study of the effects of atomic gross motion on radiation pressure and spectroscopy [5,6].

A rigorous description of atomic gross-motion effects in the presence of a radiation field has recently been given, where the dynamics of all of the particles enter the formalism on an equal footing [5]. The theory transforms the total Hamiltonian of the complete radiation-atom system into zero-order components describing the atomic internal and gross motions, as well as the radiation field, together with an interaction which is exact to all orders

of atomic polarization. The atom is defined as an aggregate composed of an arbitrary number N of particles, of charge e^ν and mass m^ν , and with laboratory-frame conjugate coordinates of \mathbf{q}^ν and \mathbf{p}^ν , where $\nu = 1, 2, \dots, N$. Since N is arbitrary, the aggregate can exhibit a net charge

$$e_T = \sum_{\nu} e^\nu, \quad (1)$$

and therefore describes an atom or ion. It is assumed that the motions of all of the particles are non-relativistic, and

$$[q_i^\mu, p_{i'}^{\mu'}] = i\hbar\delta_{ii'}\delta_{\mu\mu'}. \quad (2)$$

In dynamics invariant to a Galilean transformation the introduction of the center of mass $\mathbf{R} = \sum_{\nu}(m^\nu\mathbf{q}^\nu/M)$, where

$$M = \sum_{\nu} m^\nu \quad (3)$$

is the total atom or ion mass, is simple and unambiguous — in contrast to relativistic dynamics where several generalizations of the Newtonian definition are possible [7]. The theory is wholly quantum mechanical, with the center of mass \mathbf{R} and the total atom or ion momentum $\mathbf{P} = \sum_{\nu} \mathbf{p}^\nu$ forming the canonical commutator

$$[R_i, P_{i'}] = i\hbar\delta_{ii'}. \quad (4)$$

In the dipole approximation, to the first order in electronic charge, the total interaction truncates to the sum of the usual dipole term and the so-called Röntgen interaction. The latter plays an important role in momentum conservation in radiation pressure calculations [5] and also induces a quantum phase in a moving dipole [8].

The formalism of the theory is nontrivial and outside the scope of the present work — the reader is referred to Ref. [5] for details. Here, our interest is confined to the zero-order internal atomic Hamiltonian

$$H = \sum_{\nu} \frac{\bar{\mathbf{p}}^\nu \cdot \bar{\mathbf{p}}^\nu}{2m^\nu} + \sum_{\nu\nu'} \frac{e^\nu e^{\nu'}}{8\pi\epsilon_0|\bar{\mathbf{q}}^\nu - \bar{\mathbf{q}}^{\nu'}|}. \quad (5)$$

An important feature of (5) is that it is written in terms of internal atom or ion dynamical variables

$$\bar{\mathbf{q}}^\nu = \mathbf{q}^\nu - \mathbf{R}, \quad (6a)$$

$$\bar{\mathbf{p}}^\nu = \mathbf{p}^\nu - \frac{m^\nu}{M} \mathbf{P}, \quad (6b)$$

which, from Eqs. (2) and (4), form the noncanonical commutator

$$[\bar{q}_i^\nu, \bar{p}_{i'}^{\nu'}] = i\hbar\delta_{ii'} \left\{ \delta_{\nu\nu'} - \frac{m^{\nu'}}{M} \right\}. \quad (7)$$

The internal atom or ion phase space is separate from that of the gross motion, that is,

$$[\bar{q}_i^\nu, P_{i'}] = [R_i, \bar{p}_{i'}^{\nu'}] = 0, \quad (8)$$

and overcomplete in the sense that equations of constraint

$$\sum_\nu \bar{\mathbf{p}}^\nu = 0, \quad (9a)$$

$$\sum_\nu m^\nu \bar{\mathbf{q}}^\nu = 0 \quad (9b)$$

may be constructed for the internal variables. Nevertheless, a canonical commutator

$$[\bar{q}_i^\nu - \bar{q}_{i'}^{\nu'}, \bar{p}_{i'}^{\nu'}] = i\hbar\delta_{ii'}, \quad (10)$$

where $\nu \neq \nu'$, may be formed involving the position $\bar{\mathbf{q}}^\nu - \bar{\mathbf{q}}^{\nu'}$ of any particular particle ν relative to a different particle ν' . This is a generalization of the well-known result for a hydrogenic atom [9], where (9a) is used to eliminate one of the internal momenta, say $\bar{\mathbf{p}}^2$, with the effect that (5) reduces to the familiar Hamiltonian

$$H = \frac{\bar{\mathbf{p}}^1 \cdot \bar{\mathbf{p}}^1}{2\mu} - \frac{e \times e}{4\pi\epsilon_0 |\bar{\mathbf{q}}^1 - \bar{\mathbf{q}}^2|} + (\text{infinite energies}) \quad (11)$$

written in terms of the reduced mass $\mu = m^1 m^2 / (m^1 + m^2)$. The general Hamiltonian (5) must be read in conjunction with the noncanonical commutator (7) and the equations of constraint (9).

The non-Schrödinger representation

$$\bar{\mathbf{p}}^\nu = -i\hbar \frac{\partial}{\partial \bar{\mathbf{q}}^\nu} + i\hbar \frac{m^\nu}{M} \sum_{\nu'} \frac{\partial}{\partial \bar{\mathbf{q}}^{\nu'}} \quad (12)$$

of the internal momentum (6b) leads to a complicated eigenvalue equation for a general atom or ion. However, as mentioned earlier, a determination of the eigenfunctions is unnecessary in order to obtain the corresponding sum rule. From the Hamiltonian (5), together with the non-canonical commutator (7) and the equation of constraint (9a), one may write

$$[\mathbf{d} \cdot \boldsymbol{\epsilon}, [\mathbf{d} \cdot \boldsymbol{\epsilon}', H]] = \hbar^2 \left\{ \frac{e_T^2}{M} - \sum_\nu \frac{e^\nu e^\nu}{m^\nu} \right\} \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}', \quad (13)$$

where the dipole moment is given by

$$\mathbf{d} = \sum_\nu e^\nu \bar{\mathbf{q}}^\nu \quad (14)$$

and $\boldsymbol{\epsilon}, \boldsymbol{\epsilon}'$ are two unit vectors to be identified as the polarizations of the incident and scattered photons of the electric-dipole interaction. Finally, the TRK sum rule

$$\sum_\iota \{2\omega_\iota - \omega_\alpha - \omega_\beta\} \langle \Psi_\alpha | \mathbf{d} \cdot \boldsymbol{\epsilon} | \Psi_\iota \rangle \langle \Psi_\iota | \mathbf{d} \cdot \boldsymbol{\epsilon}' | \Psi_\beta \rangle = \hbar \left\{ \sum_\nu \frac{e^\nu e^\nu}{m^\nu} - \frac{e_T^2}{M} \right\} \boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}' \delta_{\alpha\beta}, \quad (15)$$

corrected for the atom or ion center of mass and net charge e_T , is obtained after the use of the closure relationship

$$\sum_\iota |\Psi_\iota\rangle \langle \Psi_\iota| = 1. \quad (16)$$

In (15), the internal atom or ion eigenstates $|\Psi_x\rangle$ correspond to the eigenenergies $E_x = \hbar\omega_x$, where $x = \alpha, \beta, \iota$, and the sum over ι is over all possible eigenstates consistent with (16). The right-hand side of (15) reduces to the familiar form of $(e^2/\mu)\boldsymbol{\epsilon} \cdot \boldsymbol{\epsilon}' \delta_{\alpha\beta}$ in the case of a hydrogenic atom.

Finally, adopting the results of Ref. [4], the corresponding form of (15) for an atom or ion of $s+1$ equally spaced eigenenergy levels is

$$\sum_{n=0}^s \omega \{2n - i - j\} \langle i | \mathbf{d} \cdot \boldsymbol{\epsilon} | n \rangle \langle n | \mathbf{d} \cdot \boldsymbol{\epsilon}' | j \rangle = \hbar \left\{ \sum_\nu \frac{e^\nu e^\nu}{m^\nu} - \frac{e_T^2}{M} \right\} \left\{ \delta_{ij} - (s+1)\delta_{is}\delta_{sj} \right\}, \quad (17)$$

where the eigenvalue equation $H|x\rangle = x\hbar\omega|x\rangle$, with x assuming the integers i, j , and n , defines the eigenenergies. Therefore, the off-diagonal elements of the dipole interaction for a two-level atom or ion are such that

$$|\langle 0 | \mathbf{d} \cdot \boldsymbol{\epsilon} | 1 \rangle|^2 = \frac{\hbar}{2\omega} \left\{ \sum_\nu \frac{e^\nu e^\nu}{m^\nu} - \frac{e_T^2}{M} \right\}, \quad (18)$$

with $\hbar\omega$ as the energy difference between the ground $|0\rangle$ and excited $|1\rangle$ states.

Equation (15) provides the main conclusion of this report and represents the TRK sum rule for an N -particle atom or ion, corrected for the gross motion of its center of mass.

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