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Nuclear Electric Dipole Shielding in Molecular Ions

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A formula, which includes the effects of finite nuclear masses, is derived for the force on a nucleus in a (possibly molecular) ion in a spatially uniform (possibly time dependent) electric field.

Key words: Dipole shielding.

In 1954 Foley and Sternheimer [1] showed that for a non relativistic atomic ion in a stationary state, the average force on the nucleus in the presence of a static, spatially uniform electric field $\vec{E}$ is, in the fixed nucleus approximation

$$\langle \vec{F}_1 \rangle = q\vec{E} \tag{1}$$

where q is the net charge of the atomic ion. They also showed (see also [2]) that if one takes account of the finite mass M_1 of the nucleus, then the right hand side of (1) is multiplied by

$$M_1/M \tag{2}$$

where M is the total mass of the atomic ion.

Subsequently [3–4] the result Eq. (1) was generalized by allowing $\vec{E}$ to be time dependent. It is one purpose of this note to further generalize by including the effects of finite nuclear mass. A second purpose is to broaden the scope of the whole discussion so as to include not just atomic ions but ions in general, i.e. molecular ions.

To this end it will be convenient to use the nucleus in question as the origin of all internal coordinates. Thus we introduce

$$\vec{X}_a = \vec{R}_a - \vec{R}_1 \tag{3}$$

$$\vec{X} = \left(M_1\vec{R}_1 + \sum_a M_a\vec{R}_a\right)\Big/M \tag{4}$$

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where $a = 2, 3, \ldots$ labels the electrons and any other nuclei and where M is now the total mass of the ion: $M = \sum_a M_a + M_1$ (actually, as far as the formal discussion is concerned particle 1 could be an electron or a muon or anything else as could particles $2, 3, \ldots$). Combining Eqs. (3) and (4) we then find that

$$\vec{R}_1 = \vec{X} - \frac{\sum\limits_a M_a \vec{X}_a}{M}. \tag{5}$$

To calculate $\langle \vec{F}_1 \rangle$ we employ Ehrenfest's theorem:

$$\langle \vec{F}_1 \rangle = M_1 \frac{d^2}{dt^2} \langle \vec{R}_1 \rangle. \tag{6}$$

Using Eq. (5) this becomes

$$\langle \vec{F}_1 \rangle = M_1 \frac{d^2}{dt^2} \langle \vec{X} \rangle - \frac{M_1}{M} \frac{d^2}{dt^2} \left\langle \sum_a M_a \vec{X}_a \right\rangle \tag{7}$$

which, invoking Ehrenfest's theorem again, this time for the center of mass motion, can be written as

$$\langle \vec{F}_1 \rangle = \frac{M_1}{M} \left[q\vec{E} - \frac{d^2}{dt^2} \left\langle \sum_a M_a \vec{X}_a \right\rangle \right], \tag{8}$$

where q is now the net charge of the ion. Eq. (8) is our main result. We now turn to examples.

If, with $\vec{E}$ time independent, the internal part of the wave function (we will assume that the wave function is a product of an internal wave function and a center of mass wave function in so far as the spatial dependence is concerned) is a stationary state, then the second term on the right hand side of Eq. (8) will vanish. For an atomic ion we then recover Eq. (1) with Eq. (2). Further we see that, with the proper interpretation of the symbols, the same formula also applies to a nucleus in a molecular ion. Note however that in this case the quantum-mechanical averaging involves not only electronic averaging but also nuclear averaging, i.e. vibrational and rotational averaging. Note also that the infinite mass limit of the formula for $\langle \vec{F}_1 \rangle$ is ambiguous (what does one assume about the ratios of nuclear masses?). However if we compute the average *total* force on *all* the nuclei then the result is evidently

$$\frac{M'}{M} q\vec{E} \tag{9}$$

where M' is the total mass of all the nuclei, and this, in the infinite mass limit becomes the known [5–7] result

$$q\vec{E}. \tag{10}$$

If on the other hand $\vec{E}$ is time dependent then for an atomic ion Eq. (8) clearly yields the desired generalization of the results derived in [3–4] while for a molecular ion it yields new and potentially useful relations. (For an atomic ion $\sum_a M_a\vec{X}_a = \sum_a \vec{X}_a$ is the negative of the dipole moment with respect to the nucleus. In particular, for $q=0$ if $\vec{E}$ is simple harmonic with frequency ω then through first order in $\vec{E}$

$$\frac{d^2}{dt^2}\left\langle \sum_a \vec{X}_a \right\rangle = \omega^2 \alpha(\omega)\vec{E} \tag{11}$$

where $\alpha(\omega)$ is the polarizability of the atom. More generally, from Eq. (5), one sees that $\sum_a M_a\vec{X}_a$ is proportional to the dipole moment of the chosen nucleus with respect to the center of mass of the ion.)

Thus far we have assumed that we have exact wave functions. To consider situations in which we have only approximate, variational, internal wave functions, it is useful to note that, as readily follows from the form of the internal Hamiltonian H

$$\begin{aligned} H = {} & \sum_a \frac{\vec{P}_a^2}{2M_a} + \frac{1}{2M_1}\left(\sum_b \vec{P}_b\right)^2 + \tfrac{1}{2}\sum_a \sum_{\substack{b \\ a\neq b}} \frac{q_a q_b}{|\vec{X}_a - \vec{X}_b|} \\ & + \sum_a \frac{q_a q_1}{|\vec{X}_a|} - \sum_a \left(q_a - q\frac{M_a}{M}\right)\vec{X}_a \cdot \vec{E} \end{aligned} \tag{12}$$

the static theorem is equivalent to the vanishing of $\langle H \sum_a \vec{P}_a - \sum_a \vec{P}_a H\rangle$. Here of course $\vec{P}_a$ is the momentum canonically conjugate to $\vec{X}_a$, and q_a is the charge of particle a. Thus [6] a sufficient condition that the static theorem be satisfied by an optimal variational internal wave function is that the set of trial internal wave functions be invariant to a rigid displacement of the $\vec{X}_a$. Similarly (much as in [3]) one finds that the time dependent theorem will be satisfied if in addition the set is invariant to multiplication by $\exp i \sum_a \vec{X}_a \cdot \vec{\varepsilon}$ where $\vec{\varepsilon}$ is an arbitrary vector.

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