On the ”permanent electric dipole moment” in molecules

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Abstract

The scope of this note is to discuss two opposing statements on a possible permanent electric dipole moment in molecules. Based on fundamental symmetries, I clarify why molecules cannot have a permanent electric dipole moment and nevertheless electric-dipole rotational and vibrational spectra can only be observed in heteronuclear molecules while they are missing in molecules with identical nuclei.

1 Introduction

Most texts discussing molecular spectra state that electric-dipole vibrational and rotational transitions cannot be observed in homonuclear molecules because they cannot have a permanent electric dipole while the transitions can be observed in heteronuclear molecules that would have such a permanent electric dipole moment (see, for example, [1, 2, 3, 4]). On the other hand, papers discussing the electric dipole moment of fundamental particles (see, for example, [5, 6]) state that atoms and molecules cannot have a permanent electric dipole moment unless fundamental symmetries, namely, time reversal ($T$) and parity ($P$) are violated, violations that are searched for in ongoing experiments on the electron’s electric dipole moment [7, 8, 9, 10].

The scope of this note is to reconcile these two drastically opposing statements on fundamental symmetries and clarify why molecules cannot have a
permanent electric dipole moment and why nevertheless electric-dipole rotational and vibrational spectra can be observed in heteronuclear molecules while they are missing in homonuclear molecules. I consider a simple model for neutral diatomic molecules but the main conclusion is valid also for more complex molecules including finer effects [11].

2 The electric dipole moment

The permanent electric dipole $D_{aa}$ of a molecule in a state $a$ is:

\[ D_{aa} = \langle \psi_a | D | \psi_a \rangle , \]

(1)

where the electric dipole operator $D$ in the nonrelativistic limit is given by

\[ D = e \left( \sum_i Z_i R_i - \sum_j r_j \right) , \]

(2)

with $e$ the elementary charge, the first sum running over the positions $R_i$ of the nuclei with charges $Z_i e$, and the second sum running over the positions $r_j$ of the electrons $1$. The typical argument on a possible permanent electric dipole moment in molecules and the resulting rotational and vibrational spectra goes as follows [4]: In the case of atoms, the permanent electric dipole moment is always zero for non-degenerate states because they are eigenstates of the parity operator and $D$ is odd under this transformation. The permanent electric dipole moment would be instead different from zero for heteronuclear molecules, such as $\text{HCl}$, because an excess charge would be associated to one of the nuclei compared to the other. In symmetrical homonuclear diatomic molecules, such as $\text{H}_2$, $\text{O}_2$, $\text{N}_2$, the permanent electric dipole moment is instead zero. As a consequence, rotational and vibrational spectra would only be observed for heteronuclear molecules because the transition amplitude for absorption or emission of radiation by a molecule is proportional (in the electric-dipole approximation) to the matrix element of the electric dipole operator.

This is consistent indeed with what is observed experimentally and no such spectra can be observed for homonuclear molecules but the explanation reported above is, in my opinion, misleading because molecules cannot have a permanent electric dipole moment, as discussed in the following.

According to Eq. 2 in order to have an electric dipole moment, the electrons in a molecule should move closer to one nucleus than to the other.

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1 The electric dipole moment operator is independent of the choice of the origin for neutral systems.
so that one nucleus would be negatively charged while the other would be positively charged. Even if this was the case, since there is no preferential direction in space there would be no electric dipole moment fixed in space.

Moreover, a permanent electric dipole moment for a particle at rest should be proportional to the particle spin or total angular momentum that provide a reference direction; but $D$ is even under time-reversal $T$ and odd under parity-reflection $P$ while spin is odd under $T$ and even under $P$. Therefore, according to the standard model of fundamental interactions, an elementary or composite particle, such as an atom or a molecule, cannot have a permanent electric dipole moment unless $T$ and $P$ symmetries are violated. This is the motivation for the ongoing experimental searches of an electric dipole moment in atoms and molecules that would be evidence of a non null electric dipole moment of the electron (see [7, 8, 9, 10] and references therein).

3 The "permanent electric dipole moment" in heteronuclear molecules

Let’s clarify how a permanent electric dipole moment would manifest itself and the relation with molecular spectra [5, 8].

In the presence of an external electric field $\vec{E}$, the interaction energy of a neutral particle with the field is

$$\Delta E = D_i E_i + D_{ij} E_i E_j + \ldots,$$  \hspace{1cm} (3)

The first term is linear in $\vec{E}$ and it is non null if a static electric dipole moment $D$ is present; the second term is instead due to an induced electric dipole moment which is produced by the field and interacts with the field itself so that the dependence is quadratic. So, the presence of a permanent electric dipole manifests itself with a change in energy proportional to the applied field $E$.

The reason for the misleading statement about a permanent electric dipole moment of heteronuclear molecules, stems from the presence of quasi-degenerate states with opposite parities. As is well known for the hydrogen atom, considering as degenerate the excited states with different $l$ values with parities given by $(-)^l$, the presence of an external electric field mixes states with opposite parities; this leads to a linear dependence of the energy change on the applied electric field and we can say that in this state the atom has a permanent electric dipole moment. This is strictly true only if the opposite-parity states have the same energy. If the opposite-parity states are quasi-degenerate, for weak electric fields the energy dependence is quadratic,
corresponding to an induced electric dipole moment; only when the effect of the electric field is large enough to make the energy separation between the unperturbed levels negligible, the linear behaviour is approached. So, the smaller the energy separation between nearby opposite-parity states, the larger the polarizability and the better the system can approximate the behaviour of a permanent electric dipole moment.

In the case of molecules, this effect can be produced by the electric field mixing nearby rotational states which have a parity given by \((-)^K\), where $K$ is the rotational quantum number. However, as in the case of the hydrogen atom, this is not an evidence of the presence of a permanent electric dipole moment nor an indication of $P$ and $T$ violation because if a sufficiently weak electric field is applied, the quadratic dependence shows the induced origin of the observed dipole moment. This clarifies the origin and the real meaning of the expression "permanent electric dipole moment" for heteronuclear molecules.

4 Missing rotational and vibrational spectra in homonuclear molecules

Why the argument above does not work for homonuclear molecules and they do not show even an apparent "permanent electric dipole moment" nor electric-dipole rotational and vibrational spectra?

The total molecular wave function $\psi_t$ can be written, in the Born-Oppenheimer approximation and neglecting the very small coupling of the nuclear spin with the rest of the molecule, in the form

$$\psi_t = \psi_e \psi_v \psi_r \psi_n,$$

where $\psi_e$, $\psi_v$, and $\psi_r$ are the electronic, vibrational, and rotational functions, respectively, and $\psi_n$ is the nuclear spin function. According to the symmetrization postulate of quantum mechanics and the spin-statistic connection, if the nuclei are identical and have an integer (half-integer) spin, the total wave function $\psi_t$ must be symmetric (anti-symmetric) in the exchange of two nuclei.

The electronic wave function $\psi_e$ can be either even or odd under the exchange of the nuclei. The vibrational wave function $\psi_v$ is symmetric in the exchange of the nuclei because it depends only on the magnitude of the internuclear distance.

As far as the rotational states are concerned, if the nuclei have no nuclear spin ($I=0$), alternate rotational states with even or odd rotational quantum
numbers are forbidden depending on the symmetry of $\psi_e$. This is the case, for example, of $^{16}\text{O}_2$; this effect was tested in high-sensitivity molecular spectroscopy experiments searching for possible violations of the symmetrization postulate of quantum mechanics and of the spin-statistic connection (see [12, 13, 14, 15] and references therein). As a result, the mixing by an electric field of nearby opposite-parity rotational levels is not possible in this case. If the nuclei have a nuclear spin, different rotational levels will be associated to different values of the total nuclear spin. In the case of $^1\text{H}_2$ ($I = 1/2$), for example, singlet and triplet nuclear spin functions are associated to alternate rotational states and the transitions between these states are extremely weak [16].

As a result, the mixing by an electric field of nearby opposite-parity rotational levels is virtually impossible for homonuclear molecules; thus there is no linear dependence of the energy shift on the electric field and no apparent "permanent electric dipole moment" in this case.

5 Conclusions

In conclusion, molecules, either homonuclear or heteronuclear, cannot have a permanent electric dipole moment because of $P$ and $T$ symmetries. The apparent behaviour as if a permanent electric dipole moment was present in heteronuclear molecules is correctly explained in terms of a mixing of rotational states induced by an external electric field. This mixing is not possible in homonuclear molecules due to the bosonic or fermionic nature of the nuclei.

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