

# Electric Dipole Moments Reconsidered

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## Abstract

The electric dipole moments of elementary particles, atoms, molecules and their connection to the electric susceptibility are discussed for stationary states. Assuming rotational invariance it is emphasized that for such states only in the case of a parity and time reversal violating interaction the considered particles can obtain a nonvanishing expectation value for the electric dipole moment.

# 1 Introduction

Electric dipole moments (EDM) come in many varieties like the EDM of the neutron in CP-violation, EDM-transitions in atoms, the linear Stark effect in hydrogen and the induced and permanent EDM of molecules leading to the Langevin-Debye formula [1] for the electric susceptibility. Since there exist many confusing and misleading statements about EDM in the literature it seems worthwhile to analyse more carefully their existence and emergence. Probably all this confusion is due to the time lag between the fundamental book on electric and magnetic susceptibilities by Van Vleck [2] and the much later discovery of parity [3] and time reversal [4] violation. It is therefore not astonishing, that the term permanent EDM is used in at least three different contexts; that is in connection with molecules, the Stark effect in atoms and CP-violation. Historically a permanent EDM is connected with the appearance of a term proportional to  $1/T$  in the Langevin-Debye formula, whereas the constant term in temperature is considered to be due to an induced EDM. But the electric susceptibility being the property of a macroscopic ensemble of molecules [5] does not tell anything about the property of an individual molecule in a stationary state, which only in the case of CP-violation (assuming CPT-invariance), as will be discussed in part IV, can have a real permanent EDM intrinsic to the molecule, independent of the electric field strength. Actually the polarization (or average dipole moment per unit volume) of the macroscopic ensemble of molecules is just the product of the electric susceptibility with the electric field strength, and if one would not use the terminology of the Langevin-Debye formula one would call this an induced EDM, induced in the usual sense that it does not exist without applying an electric field! In part II simple arguments are given that without violation of P and T invariance the Langevin-Debye formula can be derived of course as has been shown in much more detail in [2] and in accordance with the size of these effects, which would be much too small if they were due to P and T violation. A simple numerical example also shows that the form of the electric susceptibility at the classical level is just a result of the involved effective potentials. In part III it is argued that the linear Stark effect in hydrogen e.g., which is usually connected with announcing a permanent EDM, see [6] e.g., does lead to the same result for the electric susceptibility as the quadratic Stark effect. Therefore at the macroscopic level to both cases would be attributed a permanent EDM!

It is not claimed that all the results of this paper are new. Wherever possible a reference is given, though the list is certainly very incomplete and probably does not give due respect to priority, but even some of these references were not easy to find. Instead it is hoped that this work will contribute to clarify the role of the different uses of the term EDM and improve the understanding of the fundamental difference between the real permanent EDM due to CP-violation and all other EDM.

The convention of setting Planck's constant  $\hbar = 1$  is adopted. Furthermore only bound states of two particles of opposite charges are considered for simplicity, which means bound ions in the case of molecules, "electrons" and nucleus in the case of atoms and two quarks for "nuclei". This is already sufficient to show the weak points of many arguments.

## 2 Langevin-Debye Formula for Molecules

It is well known how to calculate the electric susceptibility  $\chi$  of molecules at a classical level without taking into account quantum mechanics [1,7]. Let  $\mu$  denote the assumed "permanent" EDM of the molecule whose origin due to the fundamental interactions is not considered. Classically it is a "real" property of an individual molecule giving to it a certain shape or better direction. Since an electric field distorts the electric charge distribution, it induces at least for weak fields an EDM proportional to its strength and let  $\alpha$  be this proportional constant called polarizability. The energy of such a molecule in an electric field with strength  $E$  parallel to the  $z$ -axes is then given by

$$U = -\mu E \cos \vartheta - \alpha E^2/2 \quad (1)$$

From this one derives the classical partition function  $Z$  by integrating over all angles that is

$$Z = \int d\Omega \exp(-\beta U) \quad \text{with } \beta = 1/kT \quad (2)$$

The electric susceptibility is then defined by

$$\chi = \frac{N}{E\beta} \frac{d}{dE} \ln Z \quad (3)$$

resulting in the Langevin-Debye formula

$$\chi = N \left( \frac{\mu^2}{3kT} + \alpha \right) \quad (4)$$

where  $N$  is the number of molecules per unit volume. In deriving formula (1) for the contribution of the "permanent" EDM the assumption  $\mu E/kT \ll 1$  has been made though the exact result can be given in terms of the Langevin function. Obviously, looking at the molecule at a classical level, there is quite a difference between the microscopic properties of an individual molecule and the macroscopic behaviour of an ensemble of molecules. For the individual molecule the energy in an electric field due to its "permanent" EDM is proportional to the field strength whereas for the ensemble of molecules the energy is proportional to the square of the field strength. Already this should make one suspicious about the physics and terminology involved because one starts with a microscopic EDM independent of any existing electric field for the individual molecule and ends up with a macroscopic EDM which exists only if an electric field is applied and should actually be called induced. But even at the classical level things become more confusing if one looks for models for the polarizability  $\alpha$ . A reasonable model should be a system of two particles with opposite charge  $e$  bound by a potential  $V(x)$  depending on their relative distance. The energy in the center of mass system in an exterior electric field is then given (in one dimension) by

$$H = H_0 - eEx \quad \text{with } H_0 = p^2/2m + V(x) \quad (5)$$

The polarizability  $\alpha$  should then be obtained from the partition function  $Z$ , now defined by

$$Z = \int dp dx \exp(-\beta H) \quad (6)$$

just like the electric susceptibility in (3) without the factor  $N$ . If one uses a harmonic oscillator potential the well known exactly calculable result is a polarizability independent of the temperature  $T$ . But this is a special feature of the harmonic oscillator potential and things change drastically for other potentials. For a potential  $V(x)$  symmetric about  $x = 0$ , which should be used because otherwise one would have a parity violating interaction, it is easy to calculate the polarizability numerically. In Fig.1 the result for a  $x^4$ -potential is compared with the harmonic oscillator result.

Of course it are not so much the actual numerical values which are of interest here but the general behaviour. The  $x^4$ -potential has evidently a region where  $\alpha$  is quite  $T$ -dependent, looking like a "permanent" EDM whereas in the low temperature region the polarizability approaches a constant value which would be considered as an induced EDM. Therefore in general the conclusion can only be that a permanent EDM leads to a  $1/T$  behaviour in the Langevin-Debye formula but that such a term can equally well arise as an induced EDM because the interaction between the charged particles is not just a pure harmonic oscillator potential.

The quantum mechanical derivation of the Langevin-Debye formula has been treated in great detail in [2]. The important result in this case is that the  $1/T$  term in the Langevin-Debye formula originates from an appropriate energy spectrum of the individual particle. This has nothing to do with parity or (and) time reversal violation and there is no necessity for a permanent EDM for an individual molecule. One can understand this quite easily in the following way. Quantum mechanically the partition function  $Z$  for the same system as considered classically (eq. 5) is given by the trace over the density matrix

$$Z = \text{Tr}(\exp(-\beta(H_0 - e\vec{E}\vec{x}))) \quad (7)$$

Since in the following effects arising from the noncommutativity of  $H_0$  with  $x$  are neglected (they are higher order effects in  $1/T$  and  $\hbar$ ) the electric susceptibility is again given by (3). If one assumes that the relevant eigenstates of  $H_0$ , denoted by  $|n\rangle$ , have the property that approximately

$$\langle n | (\vec{E}\vec{x})^{2m} | n \rangle = (\langle n | (\vec{E}\vec{x})^2 | n \rangle)^m \quad (8)$$

and

$$\langle n | x_i x_j | n \rangle = \frac{1}{3} \delta_{ij} \mu^2 \quad (9)$$

then one can evaluate the partition function  $Z$  quite easily resulting in

$$Z = \cosh(\beta E \mu / \sqrt{3}) \sum_n \exp(-\beta E_n) \quad (10)$$

But the energy eigenvalues of  $H_0$ ,  $E_n$ , are independent of the electric field  $E$  and therefore equ. 3 leads in the limit  $E\mu \ll kT$  to the expected result for the electric susceptibility

$$\chi = N \frac{\mu^2}{3kT} \quad (11)$$

Questions of parity never enter the whole argument, all is just a result of the assumed energy level structure of the considered system. It is only this structure which is responsible for the  $1/T$  term in the susceptibility and in principle any system of bound charged particles can produce such a term if the level structure is right. There is at first no difference between molecules as bound states of atoms, atoms as bound states of nucleons and electrons, and nucleons being bound states of quarks. Only their different energy level structure and the different energy ranges and necessary temperatures should be responsible for the assumed absence of a  $1/T$  term for atoms and nucleons (elementary particles).

### 3 Stark Effect and EDM

A linear Stark effect, that is a change in the energy levels of a microscopic system proportional to the electric field strength, is usually connected with a permanent EDM. This can occur only if there are degenerate energy eigenstates with opposite parity. Usually a standard example [6] is the hydrogen atom with its  $2s$  and  $2p$  energy levels. Of course this example is only academic since the fine structure of Coulomb energy levels splits states with different angular momentum. Though it looks unlikely to have real physical states of opposite parity which are degenerate in energy this cannot be excluded in principle. Due to the problems of Fermi statistics there does not even exist a proof for the uniqueness of the ground state of an atom with more than two electrons [8]. Nevertheless even if one assumes a degenerate ground state with states of opposite parity it would be very difficult to ascribe to it a definite EDM. The value of the EDM of an individual object without any interaction would depend on the production mechanism since any superposition of the two degenerate states is equally good. This is quite different to the case of a permanent magnetic moment due to spin which is an intrinsic property of a particle and therefore has a definite value. The only difference between the degenerate and nondegenerate case is the resistance to a deformation by an electric field. On a macroscopic level one would therefore not expect much difference between an exactly and an approximately degenerate case. Actually this can be seen quite easily by considering a system with two energy levels of opposite parity only. Let  $|a\rangle$  and  $|b\rangle$  denote these two eigenstates of  $H_0$ . The eigenvalues in an electric field of the total Hamiltonian  $H$ , which looks formally like (5), are then found by diagonalizing the corresponding  $2 \times 2$  matrix resulting in

$$E_{1,2} = \frac{1}{2}[(E_a + E_b) + \sqrt{(E_a - E_b)^2 + 4E^2e^2\langle x \rangle^2}] \quad (12)$$

where  $\langle x \rangle$  denotes the off-diagonal element  $\langle a|x|b \rangle$ . The partition function  $Z$  is then just the sum

$$Z = \exp(-\beta E_1) + \exp(-\beta E_2) \quad (13)$$

from which one derives in the standard way using (3) for the electric susceptibility the expression

$$\chi = \frac{2N\langle x \rangle^2 e^2}{\sqrt{(E_a - E_b)^2 + 4E^2e^2\langle x \rangle^2}} \cdot \tanh \sqrt{(E_a - E_b)^2 + 4E^2e^2\langle x \rangle^2}/kT \quad (14)$$

With the usual assumption that the numerator in the tanh-function should be small compared to  $kT$  the whole square root expression drops out and the simple result is

$$\chi = 2N(x)^2 e^2 / kT \quad (15)$$

with no difference for the degenerate ( $E_a = E_b$ ) or nondegenerate case. So the occurrence of the  $1/T$  term is again essentially the consequence of the level structure of the system and not due to an intrinsic property of an individual particle.

## 4 CP-Violation and Real Permanent EDM

It has been a well known fact for a very long time that without parity violation elementary particles can have no permanent EDM. This is no contradiction to the previous statements because now the problem of the existence of an EDM as an intrinsic property of a particle independent of any electric field is addressed. Subsequently it was therefore pointed out that the measurement of an EDM for an elementary particle would be a sign for parity violation [9]. Later on Landau [10] gave an argument that also time reversal violation is necessary for the existence of an EDM, the main point being that rotational invariance requires the EDM to be a vector and the only available vector for an elementary particle is its total angular momentum  $\vec{J}$ . Therefore the EDM must be proportional to the angular momentum and the different behaviour of the EDM and angular momentum under space and time reversal

$$\vec{\mu} \xrightarrow{P} -\vec{\mu} \quad \vec{\mu} \xrightarrow{T} \vec{\mu} \quad \vec{J} \xrightarrow{P} \vec{J} \quad \vec{J} \xrightarrow{T} -\vec{J} \quad (16)$$

requires the violation of the corresponding symmetries if the two vectors are set proportional to each other. This has been discussed in great detail in [11]. Actually the situation is more sophisticated for two reasons. First one may doubt that the angular momentum  $\vec{J}$  is the only available vector. Then it is the result of an easy exercise that for a system with definite total angular momentum any vector operator and therefore also the EDM  $\vec{\mu}$  can be replaced essentially by [12]

$$\vec{\mu} = \vec{J}(\vec{J}\vec{\mu})/j(j+1) \quad (17)$$

This shows the proportionality to  $\vec{J}$  but the scalar product between  $\vec{J}$  and  $\vec{\mu}$  re-establishes the same transformation properties between the left and right hand side of (17) under the considered discrete symmetries (16) and therefore the argument fails. Second it is now common belief that elementary particles are bound states of quarks (with the exception of leptons and gauge bosons of course) and therefore due to the internal structure parity violation may be sufficient to allow for an EDM. Actually it can be proved that this is not so and time reversal invariance must be violated too. Since it is not easy to find the proof of this in the literature a slightly modified version of the proof in [13] is given here. A nonrelativistic bound system of particles is considered. It is assumed that time reversal and rotational invariance hold and that in addition the energy levels are only degenerate due to rotational invariance. Then no stationary state can have an EDM. This can be

seen in the following way. First one notes that under the above conditions one can choose a "real" standard basis as discussed in [12]. Denoting by  $K$  the antiunitary operator of time reversal for a system of interacting particles with spin,  $K$  is given by

$$K = Y^{(S)} K_0 \quad \text{with } Y^{(S)} = \exp(-i\pi S_y/\hbar) \quad (18)$$

where  $K_0$  is the antiunitary operator of complex conjugation and  $Y^{(S)}$  denotes a rotation of spin components by  $180^\circ$ . By assumption  $K$  commutes with the Hamiltonian of the system. Since rotational invariance is assumed one can define an operator  $K_y$  of combined time reversal and rotation of  $-180^\circ$  around the  $y$ -axes

$$K_y = Y^+ K \quad \text{with } Y = \exp(-i\pi J_y/\hbar) \quad (19)$$

which commutes with the Hamiltonian,  $J^2$  and  $J_x$ . Since

$$K_y^2 = 1 \quad (20)$$

one can use  $K_y$  to create a "real" standard basis of stationary states defined by

$$K_y |\tau, j, m\rangle = |\tau, j, m\rangle \quad (21)$$

where  $\tau$  denotes all quantum numbers describing the stationary states except total angular momentum  $j$  and its  $z$ -component  $m$ . The rest is now an easy consequence of the Wigner-Eckart theorem. The EDM  $\vec{\mu}$  is a  $J = 1$  vector operator and therefore

$$\langle \tau, j, m | \mu_q | \tau, j, m' \rangle = \frac{1}{\sqrt{2j+1}} \langle \tau, j || \mu || \tau, j \rangle \langle j, 1, m', q | j, m \rangle \quad (22)$$

Taking the special case  $m = m' = j$ ,  $q = z$  in (22), due to the nonvanishing Clebsch-Gordon coefficient on the right hand side it suffices to prove that the left hand side vanishes because then the reduced matrix element must be zero and therefore the expectation values of the EDM  $\vec{\mu}$  in any stationary state vanish. But using (21) this result follows immediately from the relations

$$\begin{aligned} \langle \tau, j, j | \mu_x | \tau, j, j \rangle &= (K_y |\tau, j, j\rangle)^\dagger \mu_x K_y |\tau, j, j\rangle = \\ (K_y^\dagger \mu_x K_y |\tau, j, j\rangle)^\dagger |\tau, j, j\rangle &= -\langle \tau, j, j | \mu_x | \tau, j, j \rangle \end{aligned} \quad (23)$$

where the fact has been used that time reversal invariance requires

$$K_y (\mu_x, \mu_y, \mu_z) K_y^\dagger = (-\mu_x, \mu_y, -\mu_z) \quad (24)$$

This shows that time reversal invariance forbids any permanent EDM. Of course nowadays time reversal and CP violation are generally accepted as a very weak effect. Therefore the neutron for example may have a permanent EDM proportional to its spin and just for completeness it will be shown that this EDM also leads to a  $1/T$  behaviour of the electric susceptibility as it should be. Let the total Hamiltonian be given by

$$H = H_0 - \mu \vec{\sigma} \vec{E} \quad (25)$$

Assuming that  $H_0$  is spin independent and taking  $E$  in the  $z$ -direction, the partition function  $Z$  is given by

$$Z = \text{Tr}(\exp(-\beta H)) = \text{Tr}(\exp(-\beta H_0))\text{Tr}(\exp(\beta\mu\vec{\sigma}\vec{E})) = Z_0[\exp(\beta\mu E) + \exp(-\beta\mu E)] \quad (26)$$

where  $Z_0$  is an  $E$  independent term. Using again (3) the result for the electric susceptibility is

$$\chi = \frac{N\mu}{E} \tanh(\beta\mu E) \quad (27)$$

which for the usually assumed small values of the argument of the tanh-function results in

$$\chi = N\mu^2/kT \quad (28)$$

as expected. Of course this effect will be very small and the detection of a  $1/T$  behaviour in a neutron gas seems to be very unlikely and certainly is not the appropriate method to measure the EDM of neutrons but the point is that even if one would measure this effect, it would tell nothing at this level about time reversal violation because the same  $1/T$  behaviour, even larger than expected by time reversal violation, may be due to the structure of energy levels of the bound quark system which forms the neutron.

## 5 Conclusion

It has been shown that the  $1/T$  behaviour of the electric susceptibility being a macroscopic property of a certain thermodynamic ensemble does not tell anything about the microscopic structure of the individual elements which form this ensemble. Actually a well defined real permanent EDM for an individual molecule, atom or elementary particle in a stationary state can only exist if parity and time reversal invariance are violated and therefore should be very small. All other EDM are induced EDM and vanish without an exterior electric field or do not refer to stationary states. This is no contradiction to the usual assumption of EDM for almost any molecule except nonpolar ones. These EDM may be discussed at the level of the Born-Oppenheimer approximation for example, which is very well suited for the calculation of energy levels. But for the description of the actual form of an individual molecule this approximation does not seem to make so much sense since it fixes the positions of the different nuclei which form the molecule thus creating an asymmetry in space which is not really present. Because of this asymmetry the proof of non-existence of real permanent EDM without violation of time reversal invariance is no longer applicable. Actually the idea of a molecule with some kind of space structure, so common in chemistry, may not be applicable to an individual molecule without any interaction with its environment. One should therefore be very cautious in attributing to stationary states of molecules a permanent electric dipole moment and consider this only as a helpful picture which has nothing to do with reality and is perhaps as close to the truth as Bohr's atomic model to the real situation. Perhaps to avoid confusion

one should even change the usual nomenclature and reserve the word permanent EDM for the small EDM due to parity and time reversal violation which has been called real permanent EDM in this paper.

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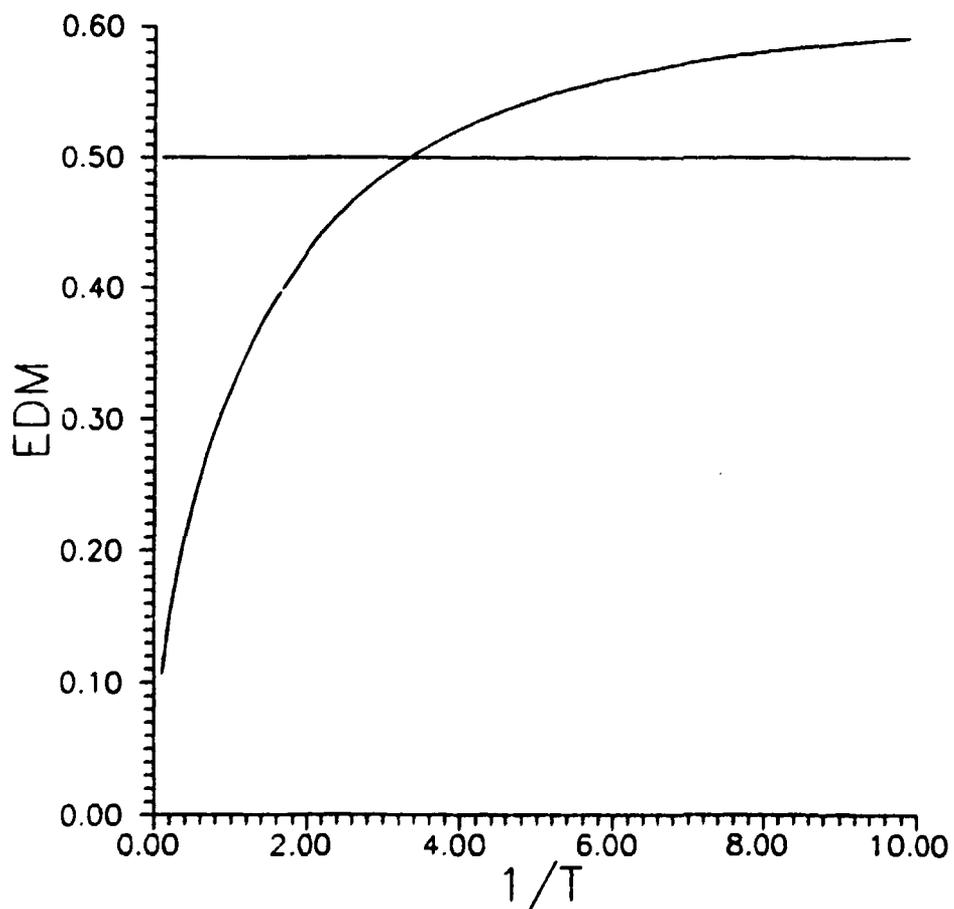


Figure 1:  
EDM for harmonic oscillator and  $x^4$  potential versus  $1/T$   
(arbitrary units)