Proposal for a sensitive search for electric dipole moment of electron with matrix-isolated radicals

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We propose using matrix-isolated paramagnetic diatomic molecules to search for the electric dipole moment of electron (eEDM). As was suggested by Shapiro in 1968, the eEDM leads to a magnetization of a sample in the external electric field. In a typical condensed matter experiment, the effective field on the unpaired electron is of the same order of magnitude as the laboratory field, typically about $10^5 \text{V/cm}$. We exploit the fact that the effective electric field inside heavy polar molecules is in the order of $10^6 \text{V/cm}$. This leads to a huge enhancement of the Shapiro effect. Statistical sensitivity of the proposed experiment may allow one to improve the current limit on eEDM by three orders of magnitude in few hours accumulation time.

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The searches for the elusive electric dipole moment of electron (eEDM) are motivated by the fact that the existence of a permanent EDM of a particle violates both parity (P) and time-reversal (T) symmetries. Due to the compelling arguments of the CPT theorem, the T-violation implies CP-violation, a subject of great interest in the physics of fundamental interactions [1]. Current experimental limit on eEDM [2] is close to the predictions in the physics of fundamental interactions [1].

The present limit on eEDM, $|d_e| < 1.6 \times 10^{-27} \text{e} \cdot \text{cm}$, is derived from a high-precision measurement [2] with a beam of Tl atoms. In such experiments one spectroscopically searches for a tiny eEDM-induced splitting of the magnetic sublevels of an atom in an externally applied electric field.

New atomic eEDM experiments plan to use optical trapping [5]. There are two other major trends aimed at improving the experimental sensitivity to eEDM: (i) employing molecules instead of atoms in spectroscopic experiments [5, 6, 7, 8] and (ii) non-spectroscopic solid state experiments [5, 9, 10, 11]. Here we propose to merge these two trends by searching for eEDM with molecules trapped in a cold matrix of rare-gas atoms (see Fig. 1).

We argue that this scheme combines advantages of both techniques. Indeed, the eEDM effects in molecules are markedly amplified because of the strong internal molecular electric field [12], much larger than attainable laboratory fields. In the present solid-state schemes the atomic enhancement of the external electric field for ions of a solid is of the order of unity [10]. By using matrix-isolated diatomic radicals, one can gain up to six orders of magnitude in the effective electric field. At the same time one retains a great statistical sensitivity of the solid-state searches. We show that this particular combination seems to drastically improve sensitivity of the eEDM search.

Let us review important aspects of the non-spectroscopic solid-state search for the eEDM. Introduced by Shapiro [13], this scheme exploits the link between EDM of the electron and it’s spin, $d = d_e \sigma$, and therefore it’s magnetic moment, $\mu_e \approx -\mu_B \sigma = -\mu_B d/d_e$. In an external E-field, because of the coupling of the eEDM to the E-field, thermal populations of the spin-up and spin-down states slightly differ, leading to the magnetization of the sample. By measuring the generated magnetic field one derives constraints on the eEDM. A proof-of-concept experiment has been carried out in 1978 by Vasiliev and Kolycheva [14]. At that time the solid-state experiment appeared to be less sensitive to the eEDM than the spectroscopic beam experiments. It is only very recently that the advances in magnetometery (see [15] and references therein) have revived an interest to the solid-state eEDM searches [5, 10, 13, 17]. Alternatively, one can look for a voltage induced in a sample in external magnetic field [11].

We focus on molecular radicals (i.e., molecules with unpaired spin) in the ground $^2\Sigma_{1/2}$ state. Consider a sample of radicals in thermodynamic equilibrium at temperature $T$. Because of the eEDM coupling to internal molecular E-field, spin substates in a molecule have slightly
different energies. This mechanism leads to a thermodynamically averaged CP-violating (P,T-odd) magnetic moment per molecule $\langle \mu_{\text{CP}} \rangle \sim \mu_B d_e E_{\text{eff}}/(k_B T)$, where $E_{\text{eff}}$ is the large molecular effective field acting on the EDM of the unpaired electron. $E_{\text{eff}}$ grows $\propto Z^3$ with the nuclear charge $Z$ of the heavier molecular constituent and one would choose to work with heavy radicals. Such molecules as BaF, YbF, HgF, and HgH belong to this broad category. We found that mercury hydride (HgH) has parameters most suitable for the proposed search, see Table I. For the HgH molecule $E_{\text{eff}} \approx 8 \times 10^{10} \text{V/cm}$ and its ESR spectrum in Ar matrix has been studied in [21].

![Scheme of searching for EDM of electron with diatomic radicals embedded in a matrix of rare-gas atoms. A polarizing electric field $E$ is applied to the matrix. As a result, molecular CP-violating magnetic moments $\mu_{\text{CP}}$ become oriented and generate ultraweak magnetic field $B^{\text{CP}}$. By measuring $B^{\text{CP}}$ one places constraints on eEDM.](image)

**FIG. 1:** Scheme of searching for EDM of electron with diatomic radicals embedded in a matrix of rare-gas atoms. A polarizing electric field $E$ is applied to the matrix. As a result, molecular CP-violating magnetic moments $\mu_{\text{CP}}$ become oriented and generate ultraweak magnetic field $B^{\text{CP}}$. By measuring $B^{\text{CP}}$ one places constraints on eEDM.

### Table I: Parameters of several heavy molecules with the matrix has been studied in [21].

| Molecule | $E_{\text{eff}}$ ($10^3 \text{V/cm}$) | $D$ (D) | $\langle n_z \rangle$ ($10^{20}$) | $n_{\text{max}}$ | $t_{\text{acc}}$ (ms) |
|----------|----------------------------------|--------|----------------------------------|----------------|------------------|
| BaF      | 8                                | 3.17   | 0.13                             | 0.03           | 300              |
| YbF      | 26                               | 3.91   | 0.16                             | 0.02           | 30               |
| HgH      | 79                               | 0.47   | 0.02                             | 1.5            | 3               |

*The effective electric field for BaF and YbF was calculated in [22, 23]. For HgH we rescale results from [21].

For diatomics, the moment $\langle \mu_{\text{CP}} \rangle$ is directed along the molecular axis. For a randomly oriented sample, however, the net magnetization would vanish. When an external E-field is applied, it couples to the traditional molecular electric-dipole moment $D$ and orients the molecules. Taking into account molecular polarization, the CP-moment can be expressed as

$$\langle \mu_{\text{CP}} \rangle \approx \mu_B d_e E_{\text{eff}}/k_B T \times \langle n_z \rangle,$$

where $\langle n_z \rangle$ is the average projection of the molecular axis onto the E-field (the field is directed along $z$-axis). Now the sample acquires a macroscopic magnetization. This magnetization generates an ultraweak magnetic field $B^{\text{CP}}$ proportional to eEDM

$$B^{\text{CP}} = 4\pi n \langle \mu_{\text{mol}}^{\text{CP}} \rangle,$$

where $n$ is the molecular number density and $\gamma$ is a geometry-dependent factor. For example, near the center of a disk-shaped sample of radius $R$ and thickness $L$, $\gamma = L/2R$.

Orientation of B-field is linked to that of the applied E-field through $\langle n_z \rangle$. Such a link is forbidden in the traditional electrodynamics. Its very presence is a manifestation of the parity and time-reversal violation. By measuring $B^{\text{CP}}$ one constrains eEDM via Eqs. (3) and (4). It is apparent that maximizing $n$ is beneficial. However, bringing radicals together is problematic — they react chemically. Here is where the matrix isolation technique becomes key. In this well-established method, the molecules are co-deposited with rare-gas atoms or other species onto a cold ($T \sim 1\text{K}$) substrate and become trapped in the matrix. Small trapped molecules exhibit properties similar to those for free molecules and a variety of studies, including determination of hyperfine-structure constants has been carried out.

There is an upper limit on the density of trapped molecules; to avoid spin alignment in the subsystem of guest molecules one requires that thermal agitations of radicals, i.e. $10^{19}$, in 1 hour.

A particular advantage of HgH is that its dipole moment is relatively small, $D = 0.47$ Debye and at $T = 1\text{K}$, the density $n_{\text{max}} \approx 1.5 \times 10^{20} \text{cm}^{-3}$.

Estimate agrees with experimental observations that 1:100 guest to host ratio is possible. According to the realistic matrix thickness and area are $L = 1\text{mm}$ and $S = 1\text{cm}^2$. That corresponds to $\gamma \approx 0.1$.

Recently developed low density plasma beam source produces permanent beam of heavy radicals with intensity $\sim 10^{13} \text{mol/sterad/s}$. Placing 1 cm² target at 20 cm from the source, one can accumulate necessary number of radicals, i.e. $10^{19}$, in 1 hour.

How are the relevant molecular properties modified by the matrix environment? A free non-rotating molecule may be described by the electronic wave function $|\Omega\rangle$, with $\Omega = \pm 1/2$ characterizing projection of spin onto molecular axis. The time-reversal operation $T$ converts
\(\Omega\)-states into each other: \(|\Omega\rangle \xrightarrow{T} | - \Omega\rangle\). In the matrix, a molecule can be considered as an individual entity perturbed by the host atoms. The local symmetry of the perturbing fields depends on the position of the molecule in the matrix. Independent of the spatial symmetry the time-reversal symmetry remains. According to the Kramers’ theorem, in the absence of magnetic fields, all levels of diatomics with half-integer spin remain two-fold degenerate for any possible electric field.

EDM interaction operates at short distances near the heavier nucleus. Expanding the electronic wavefunction in partial waves we notice that contribution to the eEDM signal of total angular momenta beyond \(s_{1/2}^-\) and \(p_{1/2}^-\) waves are strongly suppressed because of the growing centrifugal barrier and properties of the eEDM \(\Omega\). The truncated wave function has the \(C_{\infty v}\) symmetry and \(\Omega\) still remains a good quantum number for the degenerate states of matrix-isolated radicals. Within this approximation, the effective molecular Hamiltonian in the external field \(E\) reads

\[
H_{\text{eff}} = -D \cdot E^* + 2d_eE_d\Omega, \quad (5)
\]

where \(E^*\) is microscopic E-field, for small fields \(E^* = E/\varepsilon\). We used \(H_{\text{eff}}\) to arrive at Eq. \(\langle \mu_{\text{mol}}(\text{HgH})\rangle < 1.4 \times 10^{-12}\langle n_z\rangle \mu_B\), \(n\mu\).

It is instructive to compare this value to the permanent molecular CP-violating magnetic moment introduced by us in Ref. \(\text{[15]}\). This moment arises due to a magnetization of the molecule by its own electric field (irrespective of the temperature). The largest \(\mu_{\text{CP}}\) for diamagnetic molecules was found for BiF for which \(\mu_{\text{CP}} < 3 \times 10^{-17}\langle n_z\rangle \mu_B\), much smaller than the thermally-induced CP-odd moment \(\langle \mu_{\text{mol}}(\text{HgH})\rangle\). Therefore here we may neglect the permanent \(\mu_{\text{CP}}\).

An important parameter entering \(\langle \mu_{\text{mol}}\rangle\) is the degree of molecular polarization \(\langle n_z\rangle\) in the external E-field. Free diatomic molecules can be easily polarized by the laboratory fields \(\sim 10^4\text{V/cm}\), but there is a paucity of data on polarizing matrix-isolated molecules \(\text{[33]}\). Certainly, the rotational dynamics of the guest molecule is strongly affected by the matrix cage. The molecular axis evolves in a complex multi-valley potential, subject to the symmetry imposed on the molecules by the matrix cage. Depending on the barrier height between different spatially oriented valleys, the guest molecule may either execute hindered rotation or librations about the valley minima. Ref. \(\text{[32]}\) reports evidence for hindered rotation of HXeBr and Ref. \(\text{[33]}\) suggests that other hydrides can rotate. Note also, that for Ar matrix the cell size is 4.5Å, while internuclear distance for HgH is only 1.7Å. That gives us a confidence that the HgH radical can be polarized by the external electric field.

We will distinguish between two limiting cases of molecular polarization: strong and weak fields. In the former limit \(\langle n_z\rangle \sim 1\), and in the latter,

\[
\langle n_z\rangle = \frac{1}{Z_\pi} \sum_{n_z} n_z \exp \left( \frac{DE^* \langle n_z \rangle}{k_BT} \right) \approx \frac{DE^*}{k_BT} \langle n_z^2 \rangle. \quad (7)
\]

For isotropic orientational distribution, characteristic for the polycrystalline matrices, \(\langle n_z^2 \rangle = 1/3\), and we get

\[
\langle \mu_{\text{mol}} \rangle \approx \frac{1}{3} \mu_B \frac{DE^* E_{\text{edf}} d_e}{k_BT}. \quad (8)
\]

The dielectric constant of the rare-gas matrix is close to unity, but addition of polar molecules results in

\[
\varepsilon \approx 1 + 4\pi n\alpha = 1 + 4\pi n \frac{D^2 \langle n_z^2 \rangle}{k_BT} \approx 1 + \frac{4\pi n}{3} \frac{D^2}{k_BT}, \quad (9)
\]

where \(\alpha\) is molecular polarizability. For maximum density \(\langle \mu_{\text{mol}}(\text{HgH})\rangle < 1.4 \times 10^{-12}\langle n_z\rangle \mu_B\).
this field is not correlated with the direction of the external E-field and it is the main source of the noise. In our case, the signal-to-noise ratio is

\[
S/N = 3 \frac{(%mu_{CP})}{%mu_B} \sqrt{\frac{N}{\tau}},
\]

(11)

where \(N\) is the number of molecules, \(t\) is the observation time, and \(\tau\) is the correlation time for the random thermal magnetization. Factor 3 at the right hand side appears because of the averaging of the magnetic moment over orientations of the molecular axis \(n\).

For a strong spin-rotation coupling, as in the case of HgH, \(\tau\) is determined by interaction of molecular axis with environment. One of such mechanisms is the dipolar interaction between guest radicals, so that \(\tau \sim h/(D^2n)\) for the field 10 kV/cm. By integrating the signal of competing SUSY models.

important new level and, in particular, testing predictions several orders of magnitude. That will allow constraining the “new physics” beyond the Standard Model at an important new level and, in particular, testing predictions of competing SUSY models.

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