Parity violation effects in diatomics

M G Kozlov† and L N Labzowsky‡

† Petersburg Nuclear Physics Institute, 188350, Gatchina, Russia
‡ Department of Physics, Petersburg State University, 198904, St. Petersburg, Russia

Abstract. Discussion of the parity violation and the break of the time-reversal invariance in diatomic molecules has continued for a number of years. Experiments on the TlF molecule gave one of the most stringent limits on the electric-dipole moment of the proton and on the T-violating nuclear forces. At present, a new generation of experiments with paramagnetic diatomic molecules is underway. These experiments are aimed mainly at the search for the electric-dipole moment of the electron.

In this topical review we examine theoretical aspects of parity non-conservation in diatomic molecules. We focus on molecular theory leaving aside the nuclear part of the problem. In this approach the nucleus is characterized by the number of P-odd and P, T-odd moments, namely anapole moment, Schiff moment and magnetic quadrupole moment. Molecular theory has to link these moments to the experimentally measured quantities, such as frequency shifts, etc. The other possible sources of the parity non-conservation in molecules are the electron–nuclear neutral current interactions and the electric-dipole moment of the electron. They are also discussed in this review.

1. Introduction

Since the discovery of the unified electroweak theory the investigation of parity violation or parity non-conservation (PNC) effects became one of the leading problems in atomic and molecular physics. A number of reviews written on the subject were devoted mainly to atomic effects. A molecular PNC was discussed in a book by Khriplovich (1991) and, to some extent, in the recent reviews by Hunter (1991) and by Mårtensson-Pendrill (1992). The consequences for the theory of the fundamental interaction following from the atomic and molecular experiments are discussed in the review of Barr (1993). The purpose of this review is to consider the latest development in the area, restricting to diatomics which seem to be one of the closest goals for the new experiments in the near future.

PNC physics begins with the discovery of the space-parity violation (P-odd effects) in the weak interaction process of β-decay of the nuclei (Lee and Yang 1956). Then follows the observation of the space-parity and time-reversal violation (P, T-odd) effects in the decay of the neutral K-mesons (Christenson *et al* 1964). Due to the known *CPT*-conservation law (*C* is the charge conjugation) *P*- and *T*-violation also means *CP*-violation.

A new era in PNC§ physics began after the creation of the unified electroweak theory, which was completed in 1974 mainly due to the works of Glashow (1961), Weinberg (1967, 1972) and Salam (1968). The very important feature of this theory is the existence of the so-called neutral currents, i.e. the direct weak interactions between the particles, for example, between electrons and nucleons, or between two electrons. Unlike the case of β-decay these interactions do not change the charge of the particles and are caused by the exchange of

§ We use the term PNC for P-violation with and without T-violation. To distiguish between them the terms P-odd and P, T-odd are used.

heavy neutral Z-bosons now discovered experimentally (Arnison *et al* 1983, Banner *et al* 1983).

This means, that the weak interactions and, consequently, PNC effects, are present and, in principle, could be observed in every process in atomic, molecular or solid state physics. However, due to the smallness of these effects their observation is possible only under special conditions. An important step was made by Bouchiat and Bouchiat (1974) who showed that the *P*-odd electron–nucleus interactions are strongly enhanced in heavy atoms and molecules due to the high value of the electron density at the nucleus. The other standard source of PNC enhancement is the closeness of the levels of opposite parity, which results in strong mixing of these levels by PNC interactions. Later a series of successful experiments were made on heavy atoms which confirmed the existence of *P*-odd effects in atomic physics and helped to measure one of the fundamental constants of the weak interaction. A full account on the experimental situation of PNC effects in atoms can be found, for example, in a book by Khriplovich (1991) and in the recent reviews by Hunter (1991) and Barr (1993).

The consideration above mainly concerns the *P*-odd interactions. A situation with *P*, *T*-odd forces differs significantly, since up to now no closed theory has been developed for these interactions. It was understood early on that the existence of the electric-dipole moment (EDM) d for any closed system (i.e. for any free particle) means *P*, *T*-violation. Indeed, the vector d should be oriented along the unique mechanical vector characterizing the system—that is total angular momentum, or spin S of the particle. Vector d is *P*-odd and *T*-even, but S is *P*-even and *T*-odd, and the proportionality $d \sim s$ requires *P*, *T*-violation. However, the intensive search for the EDM of the atoms, molecules and neutrons, undertaken in the last few decades, has not led (up to now) to the discovery of the EDM, resulting in upper bounds for the EDM of different quantum systems. The most direct experiment for the search for the EDM is the observation of the linear Stark effect in an external electric field. The experiments with the neutral particles—atoms, molecules and neutrons—are much simpler since they are not wiped out by the applied electric field. Knowing the EDMs for atoms d_{at} and molecules d_{mol} (or the upper bounds for them) one can draw a conclusion about the EDMs of the constituent particles—electrons (d_e) and nucleons (d_p and d_n).

After the construction of the unified electroweak theory it became clear that the experimental consequences of the existence of the EDMs of the electron and the nucleons are equivalent to the consequences of the existence of the *P*, *T*-violating neutral-current interaction between the electron and the nucleus. The linear Stark effect experiments simultaneously give the upper bounds for the EDMs of the particles and for the constants of these interactions.

To the best of our knowledge the first discussion of PNC effects in molecules was by Bradley and Wall (1962) who measured the circular dichroism in the O_2 molecule and established an upper limit for the mixing of the levels of opposite parity. The systematic investigation of PNC effects in molecules began with the works of Sandars (1967) who noticed that in the TlF molecule the effect of the proton EDM is strongly enhanced due to the existence of the strong internal electric field in the polar molecules. Alternatively, one can say that the PNC effects are enhanced due to the closeness of the rotational levels of opposite parity. This paper gave a start to a series of theoretical and experimental works on the TlF molecule (Harrison *et al* 1969, Hinds *et al* 1976, Hinds and Sandars 1983, Wilkening *et al* 1984, Cho *et al* 1989, 1991) that led to one of the best upper bounds for d_p. TlF molecule experiments, however, are not sensitive to d_e, since TlF has closed shells and the total electron spin is zero to a good approximation.

The first 'naive' attempt to consider *P*-odd effects in diatomic molecules with non-

closed shells was made by Onishuk (1967) even before the discovery of neutral currents. In this work the closeness of the Λ-doublet sublevels of opposite parity was used, but the estimates, based on the charged-current interaction of the β-decay type, were not realistic. In a more detailed way the same problem was discussed by Gaizago and Marx (1974).

A new development of the PNC theory for non-closed-shell diatomics with the ground state $^2\Pi_{1/2}$ was achieved in the papers by Labzowsky (1978), where P-odd neutral-current interactions and Λ-doublets were considered, by Sushkov and Flambaum (1978) where the relativistic treatment in terms of Ω-doubling was used and also P, T-odd effects were discussed, and by Gorshkov *et al* (1979) where P- and P, T-odd effects were studied for the PbF molecule which is one of the candidates for future experiments.

A number of papers concerning the preparation of the beam experiment for the search of the EDM in the closed and non-closed shell heavy diatomics (TlF, PbF, PbI, HgF) were published by the St Petersburg group (Varentsov and Yashuk 1983, Varentsov *et al* 1985, Varentsov *et al* 1986, Ashkinadzi *et al* 1991).

In the works by Sushkov *et al* (1984) and Flambaum and Khriplovich (1985) the P- and P, T-violating interactions were considered for molecules with the $^2\Sigma_{1/2}$ ground state and, in particular, for one of the most promising, the HgF molecule. Kozlov (1985) also considered the HgF molecule and performed the first semi-empirical calculation of the molecular PNC enhancement factors. Recently the same method was applied by Kozlov and Ezhov (1994) to the YbF molecule. A dipole moment experiment on this molecule is now being prepared (Sauer *et al* 1994).

A numerical calculation of the P- and P, T-odd interaction constants within the semi-empirical treatment of the spin–orbital mixing for the PbF molecule was made by Kozlov *et al* (1987). Later these attempts were continued by Dmitriev *et al* (1992), where *ab initio* calculations of PNC interaction constants were performed with the use of the effective core potential (ECP) method. Kozlov *et al* (1991) also considered possible P-odd effects for the diatomic molecules in the external magnetic field: splitting of the radio-frequency resonance and P-odd Faraday effect.

A number of theoretical papers were also devoted to the PNC effects in polyatomic molecules, in particular in mirror molecules. There was also some speculation on the role of the PNC effects on the asymmetry of biological molecules. We do not include these problems in our review and will concentrate on PNC in diatomics. A discussion of the PNC effects in polyatomic molecules can be found in Khriplovich (1991).

2. P- and P, T-odd interactions

2.1. P-odd neutral-current e–N interactions

The effective PNC potential arising due to the neutral-current interaction of the atomic electron with the nucleon in the approximation of the infinitely heavy nucleon can be written as (see, for example, Khriplovich 1991)

$$V_{eN}^P = \frac{G_F \alpha}{\sqrt{2}} (-g_{eN}^{P1} \gamma_5^e + g_{eN}^{P2} \alpha^e \sigma^N) \delta(r) \tag{2.1}$$

where the indices e and N correspond to the electron and the nucleon; $G_F = 1.024 \times 10^{-5}/m_p^2$ is the Fermi constant of the weak interactions; m_p is the proton mass; α is the fine structure constant; γ_5 and α are the Dirac matrices; $\sigma = (\sigma_1, \sigma_2, \sigma_3)$ are the Pauli matrices; g_{eN}^{P1}, g_{eN}^{P2} are the weak interaction parameters for the proton and neutron ($N = p, n$). Atomic units are used throughout the paper.

In the unified electroweak theory

$$g_{ep}^{P1} = \tfrac{1}{2}(1 - 4\sin^2\theta_W) \qquad g_{eN}^{P1} = -\tfrac{1}{2}$$

$$g_{ep}^{P2} = -g_{eN}^{P2} = -\tfrac{1}{2}\lambda(1 - 4\sin^2\theta_W) \tag{2.2}$$

$$\lambda \simeq 1.25 \qquad \sin^2\theta_W \simeq 0.23$$

where θ_W is the Weinberg angle. Note that this value of θ_W leads to the small size of all constants except g_{eN}^{P1}.

2.2. Effective P-odd potentials

Averaging the potentials (2.1) over the nuclear variables one obtains the following PNC potential for the electron–nucleus interaction:

$$V^P = V_1^P + V_2^P = \frac{G_F\alpha}{\sqrt{2}}(-Zg_1^P(Z,N)\gamma_5^e + g_2^P(Z,N)\alpha^e I)n(r) \tag{2.3}$$

where Z and N are the numbers of protons (neutrons) in the nucleus, I is the nuclear spin, $n(r)$ is the nuclear density distribution, $n(r) = \delta(r)$ in the case of the pointlike nucleus. The functions $g_i^P(Z,N)$ are defined as

$$Zg_1^P(Z,N) = Zg_{ep}^{P1} + Ng_{eN}^{P1} \tag{2.4a}$$

$$\langle\Psi_N|I|\Psi_N\rangle\, g_2^P(Z,N) = \tfrac{1}{2}\langle\Psi_N|g_{ep}^{P2}\sum_{i=1}^{Z}\sigma_i^{(p)} + g_{eN}^{P2}\sum_{i=1}^{N}\sigma_i^N|\Psi_N\rangle \tag{2.4b}$$

where Ψ_N is the wavefunction of the nucleons in the nucleus.

According to (2.2)

$$g_1^P = \frac{1}{2} - \frac{N}{2Z} - 2\sin^2\theta_W\,.$$

For heavy atoms $g_1^P \simeq -0.75$. The quantity $Q_W \equiv 2Zg_1^P$ is sometimes called the 'weak charge' of the nucleus.

Potentials (2.3) have the following characteristic properties. First, these potentials are short-range. The Dirac electron wavefunction at the nucleus behaves like

$$\psi_{nlj} \sim r^{\gamma_j - 1} \qquad \gamma_j = \sqrt{(j+1/2)^2 - (\alpha Z)^2} \tag{2.5}$$

where n, l and j are the usual one-electron quantum numbers. Then the strongest mixing occurs for the two states with opposite parities and $j + j' = \min$, i.e. for $s_{1/2}$ and $p_{1/2}$ states.

The other characteristic property is the dependence of the potential V_2^P on the nuclear spin. This potential plays the role of a parity violating hyperfine interaction. In many-electron systems it can mix up the states with the different total electron angular momenta. It is also important to stress that the matrix elements of the potentials $V_{1,2}^P$ between the states with the opposite parities are pure imaginary.

In the non-relativistic limit (2.3) transforms to

$$V^P = \frac{G_F\alpha^2}{2\sqrt{2}}((Zg_1^P\sigma^e + g_2^P I)[p,\delta(r)]_+ - ig_2^P(\sigma^e \times I)[p,\delta(r)]_-) \tag{2.6}$$

where $[\cdots]_\mp$ denote the commutator and anticommutator. Even for $\alpha Z \ll 1$ equation (2.6) is only valid for the states with $j = \tfrac{1}{2}$. As it follows from (2.5) the atomic matrix elements of the potential (2.6) turn to zero when $j > \tfrac{1}{2}$ while the operator (2.6) also has a non-zero matrix element between $s_{1/2}$ and $p_{3/2}$ states.

2.3. Anapole moment of the nucleus

The potential V_2^P may arise not only from the neutral-current electron–nucleus interaction but also as the usual electromagnetic interaction of the electron with the anapole moment of the nucleus (Flambaum and Khriplovich 1980). The anapole moment of the particle, first introduced by Zel'dovich (1957), looks like

$$a = -\pi \int dr\, r^2 j(r)$$

where $j(r)$ is the current density distribution inside the particle. Repeating the consideration used earlier for the EDM and taking into account that vector a is P-odd and T-odd, we conclude that the proportionality $a \sim S$ violates the space-parity. Hence, the anapole moment of the nucleus arises as a result of P-odd weak interactions (both neutral and charged-current interactions) between the nucleons.

The interaction of the anapole moment of the nucleus with the electromagnetic field, produced by atomic electrons at the nucleus, results in an effective potential that looks exactly like V_2^P. Below we shall suppose that the constant g_2^P includes the contribution of the anapole moment of the nucleus.

The estimates show that the corresponding constant is larger than that produced by the neutral-current interaction, but is much smaller than the weak charge of the nucleus Q_W. Thus, in principle, $V_1^P \gg V_2^P$ and the anapole moment interaction can be only observed in special cases when for some reason the interaction V_1^P is suppressed. We shall see that, in particular, this situation takes place for diatomic molecules.

2.4. P, T-odd neutral-current e–N interaction

P, T-odd neutral-current e–N interactions can be constructed by analogy with P-odd interactions. The effective P, T-odd potentials look like

$$V^{P,T} = V_1^{P,T} + V_2^{P,T} = \frac{iG_F\alpha}{\sqrt{2}}(Zg_1^{P,T}\gamma_0^e\gamma_5^e + g_2^{P,T}\gamma^e I)n(r) \tag{2.7}$$

where $g_{1,2}^{P,T}$ are the interaction constants. Though not much is known about the order of magnitude of these constants (see Barr 1992 for details) we may again suppose, using the analogy with P-odd interactions, that $g_1^{P,T} \simeq g_2^{P,T}$ and, consequently, $V_1^{P,T} \gg V_2^{P,T}$. The non-relativistic limit of (2.7) is

$$V^{P,T} = \frac{G_F\alpha^2}{2\sqrt{2}}(i(Zg_1^{P,T}\sigma^e + g_2^{P,T}I)[p, \delta(r)]_- + g_2^{P,T}(\sigma^e \times I)[p, \delta(r)]_+). \tag{2.8}$$

The existence of the potential $V^{P,T}$ leads to the linear Stark effect in an atom or molecule in the external field $\mathcal{E}_{ext}$:

$$\Delta E_{St}(V^{P,T}) = 2\sum_{n\neq0} \frac{\langle 0|r\mathcal{E}_{ext}|n\rangle\langle n|V^{P,T}|0\rangle}{E_0 - E_n} \tag{2.9}$$

where r is the radius vector of the electron and the sum runs over the states $|n\rangle$ with opposite parity. Here for simplicity we only consider one-electron systems. Generalization to the many-electron case is trivial since all the operators involved are of the one-electron type.

Note, that the matrix elements $\langle V^{P,T}\rangle$, unlike the matrix elements $\langle V^P\rangle$, are real.

2.5. *Electric-dipole moment of the electron*

The same effects which follow from the existence of the $V_1^{P,T}$ interaction can be produced by the EDM of the electron. In principle, the interaction of the EDM of an electron with the external electric field looks like

$$H_d = -d_e \mathcal{E}_{ext} \qquad d_e = d_e \gamma_0 \Sigma \qquad \Sigma = \begin{pmatrix} \sigma & 0 \\ 0 & \sigma \end{pmatrix}.$$

However, if we consider the EDM of any charged particle (electron) inside the neutral system (atom, molecule), the internal electrostatic forces compensate the external force acting on the charged particle; otherwise the electron and the whole system should be moved by the electric field which cannot occur for neutral systems.

This means that we should look for the total interaction that is zero:

$$-\langle 0|d_e \mathcal{E}_{ext}|0\rangle - 2\sum_{n\neq 0} \frac{\langle 0|r\mathcal{E}_{ext}|n\rangle\langle n|d_e \mathcal{E}_{int}|0\rangle}{E_0 - E_n} = 0 \tag{2.10}$$

where the operator $\mathcal{E}_{int} = -\nabla U$ and U is the internal electrostatic potential. The second term in (2.10) represents the interaction of EDM with the internal electric field arising due to the polarization of the system in the external field.

Equation (2.10) is known as Schiff's theorem (Schiff 1963). It holds in the frames of the non-relativistic quantum mechanics and can easily be proved if we write down the matrix element $\langle n|d_e \mathcal{E}_{int}|0\rangle$ as

$$\langle n|d_e \mathcal{E}_{int}|0\rangle = -\mathrm{i}\langle n|d_e[p, H_0]_-|0\rangle = \mathrm{i}(E_0 - E_n)\langle n|d_e p|0\rangle \tag{2.11}$$

where H_0 is the Schrödinger Hamiltonian of the atom (molecule), p is the electron momentum operator. Inserting the expression (2.11) in the left-hand side of (2.10), using the quantum mechanical commutation relations for r and p operators and the closure relation for the eigenstates $|n\rangle$ of the H_0 operator, we immediately obtain zero.

However, Schiff's theorem is violated if the relativistic effects are taken into account. The reason is that the relativistic treatment includes magnetic forces which also take part in the equilibrium, i.e. the resultant electric field at the electron is non-zero. The residual EDM of an atom or molecule, caused by the EDM of the bound electron, appears to be even strongly enhanced compared to the free-electron EDM (Sandars 1965, 1966). This residual EDM and the corresponding Stark effect can be written down explicitly if we use the relation (see Khriplovich 1991)

$$\langle n|\Sigma\mathcal{E}_{int}|0\rangle = \mathrm{i}\langle n|[\Sigma p, H_0]_-|0\rangle$$

where H_0 is now the Dirac–Coulomb Hamiltonian, i.e. the relativistic many-electron Hamiltonian with Coulomb interaction between the electrons†. Then the residual EDM interaction with internal electric field looks like

$$V^d = -d_e(\gamma_0 - 1)\Sigma\mathcal{E} \tag{2.12a}$$

and the corresponding linear Stark splitting is

$$\Delta E_{St}(d_e) = -2d_e \sum_{n\neq 0} \frac{\langle 0|r\mathcal{E}_{ext}|n\rangle\langle n|(\gamma_0 - 1)\Sigma\mathcal{E}_{int}|0\rangle}{E_0 - E_n} - d_e\langle 0|(\gamma_0 - 1)\Sigma\mathcal{E}_{ext}|0\rangle. \tag{2.12b}$$

The high value of the electron density at the nucleus leads to the enhancement of the electron EDM in heavy atoms. The second term in the right-hand side of (2.12b) does not contain

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† More accurately, this interaction should be a projected Coulomb interaction written in the 'no virtual pair' approximation (Sucher 1980).

this enhancement and for this reason is much smaller. The other possible source of the enhancement is the presence of the small energy denominators in the sum over n in (2.12b). In particular, this takes place in diatomics, where $E_0 - E_n$ may be of the order of the molecular rotational constant. Moreover, in this case the Stark matrix elements $\langle 0|r\mathcal{E}_{ext}|n\rangle$ may be comparable with $E_0 - E_n$ and the non-perturbative treatment of the Stark effect is required.

2.6. *Electric-dipole moment of the nucleus*

Schiff's theorem prevents also the direct observation of the EDM of the nucleus d_N:

$$-d_N\mathcal{E}_{ext} - 2\sum_{n\neq0} \frac{\langle 0|r\mathcal{E}_{ext}|n\rangle\langle n|d_N\mathcal{E}_{int}|0\rangle}{E_0 - E_n} = 0. \tag{2.13}$$

In this case the main residual effect arises due to the difference between the charge and EDM distributions ρ_q and ρ_d inside the nucleus (Schiff 1963). We have to replace the interaction $-d_N\mathcal{E}_{int}$ by

$$V^S = -d_N \int [\rho_d(r') - \rho_q(r')]\mathcal{E}_{int}(r')\,dr' \tag{2.14}$$

where both ρ_q and ρ_d are normalized to unity.

The one-electron operator $\mathcal{E}_{int}(r')$ looks like $\mathcal{E}_{int}(r') = \nabla'\frac{1}{|r-r'|}$. Expanding this expression in powers of r'/r and retaining only the lowest non-vanishing contribution of order $(r'/r)^2$, one can replace (2.14) by the contact-type interaction of the electrons with the Schiff moment S of the nucleus:

$$V^S = (S\nabla)\delta(r) \tag{2.15a}$$

$$S = -\tfrac{2}{3}\pi d_N \int [\rho_d(r') - \rho_q(r')](r')^2\,dr'. \tag{2.15b}$$

Expression (2.15a) can be used with the non-relativistic wavefunctions as well as with the Dirac functions for the finite nucleus. For the latter case one can also use the more accurate expression which does not include expansion in powers of r'/r (Mårtensson-Pendrill 1992)

$$V^S = -d_N \frac{r}{r^3} \int_0^r [\rho_d(r') - \rho_q(r')]\,dr'. \tag{2.15c}$$

For $r \gg r_N$, where r_N is the nuclear radius, here the integral vanishes because of the normalization condition for densities.

In the case of a nucleus with one valence proton within the shell model of the nucleus the Schiff moment looks like (Khriplovich 1991)

$$S = d_p r_N^2 \frac{4\pi(K + 1)}{25I(I + 1)}I \tag{2.16}$$

where $K = (-1)^{I+1/2-l}(I+\tfrac{1}{2})$ and l is the orbital angular momentum of the valence proton. The additional assumption in the derivation of (2.16) is that $r_q^2 = r_d^2 = \tfrac{3}{5}r_N^2$, where r_q^2 and r_d^2 are, respectively, the mean-square radii of the charge and dipole distributions inside the nucleus. Note that this expression vanishes for $I = \tfrac{1}{2}$ and $l = 0$.

The residual interaction of the atomic EDM with the external electric field is

$$\Delta E_{St}(S) = 2\frac{S}{I}\sum_{n\neq0} \frac{\langle 0|r\mathcal{E}_{ext}|n\rangle\langle n|I\nabla\delta(r')|0\rangle}{E_0 - E_n}. \tag{2.17}$$

Note that the Schiff moment of the nucleus may also arise due to the P, T-violating interactions between the nucleons inside the nucleus (Khriplovich 1991).

2.7. Magnetic quadrupole moment of the nucleus

Equations (2.15) hold equally for paramagnetic and diamagnetic atoms and molecules. However, for non-closed shell (paramagnetic) systems there is another way of producing atomic EDM from the nucleon (proton) EDM. It is the interaction of the magnetic quadrupole moment (MQM) of the nucleus with the magnetic field of the electrons. This method usually appears to be more effective (Khriplovich 1976).

The MQM tensor for an arbitrary system is defined as

$$M_{i,k} = \int dr (r_i \epsilon_{k,n,m} + r_k \epsilon_{i,n,m}) r_n j_m \tag{2.18}$$

where j_m is the component of the internal current distribution, $\epsilon_{k,m,n}$ is the unity antisymmetric tensor. The proportionality should hold:

$$M_{i,k} \sim \left(I_i I_k + I_k I_i - \tfrac{2}{3}\delta_{i,k} I(I+1)\right) \equiv T_{i,k} \tag{2.19}$$

where I is the total spin of the system, since the tensor $T_{i,k}$ in (2.19) is the unique second-rank irreducible tensor which can be constructed from the components of the vector I. Comparing (2.18) and (2.19) one can see that the existence of $M_{i,k}$ violates P- and T-invariance.

The MQM $\mathcal{M}$ can be defined by analogy with the electric-quadrupole moment:

$$M_{i,k} = \frac{3}{2} \frac{\mathcal{M}}{I(2I-1)} T_{i,k} . \tag{2.20}$$

For nuclei with one valence proton calculations give (Khriplovich 1976)

$$\mathcal{M} = \frac{\alpha d_p}{m_p} \frac{(2I-1)(\tfrac{1}{2} - K)}{I+1} \tag{2.21}$$

where K was defined in (2.16).

The interaction of the MQM with the electron magnetic field looks like

$$V^{\mathcal{M}} = M_{i,k} F_{i,k} \tag{2.22}$$

where $F_{i,k}$ is a P, T-odd electronic tensor

$$F_{i,k} = \tfrac{1}{2}\alpha_m \nabla_n (\epsilon_{m,n,i}\nabla_k + \epsilon_{m,n,k}\nabla_i)\frac{1}{r} .$$

Since the interaction $V^{\mathcal{M}}$ is magnetic it does not obey Schiff's theorem. Then the linear Stark effect produced by this interaction is

$$\Delta E_{St}(V^{\mathcal{M}}) = 3 \frac{\mathcal{M}}{I(2I-1)} \sum_{n \neq 0} \frac{\langle 0|r\mathcal{E}_{ext}|n\rangle \langle n|T_{i,k}F_{i,k}|0\rangle}{E_0 - E_n} . \tag{2.23}$$

Due to the presence of the α matrix in $V^{\mathcal{M}}$ this interaction only works for paramagnetic atoms and molecules. As was mentioned above, usually

$$\Delta E_{St}(V^{\mathcal{M}}) \gg \Delta E_{St}(V^{S}) . \tag{2.24}$$

Again we should note that the P, T-violating interactions between the nucleons inside the nucleus also give rise to the nucleus MQM (see Khriplovich 1991).

3. Selection rules for PNC operators

3.1. Coupling schemes

The main advantage of using molecules instead of atoms is the existence of the close spin–rotational levels of opposite parity. It is also important that the spin–rotational levels of the electron vibrational ground state have narrow widths.

Below we are going to discuss selection rules for matrix elements of P-odd and P, T-odd operators between spin–rotational levels of polar diatomic molecules. First of all we shall briefly review the main coupling schemes and corresponding molecular quantum numbers for diatomics (for the details see, for example, Herzberg (1957) or Landau and Lifshitz (1979)).

In analogy with atoms where states are classified by the orbital angular momentum L, electron spin S and total electronic angular momentum j, for diatomic molecules the corresponding projections on the molecular axis are defined as

$$\Lambda = \langle L \cdot n \rangle \qquad \Sigma = \langle S \cdot n \rangle \qquad \Omega = \langle j_e \cdot n \rangle \tag{3.1}$$

where angular brackets mean averaging over the electronic state, j_e is used instead of j to distinguish it from the total angular momentum of the molecule and n is the unit vector directed along the molecular axis from the positively charged atom to the negative one. If quantum numbers Λ and Σ are well defined, then $\Omega = \Lambda + \Sigma$.

Three Hund's coupling cases correspond to the different relative strength of the spin–axis, spin–orbit and spin–rotation interactions:

Case a. The spin–axis interaction dominates. In this case all three quantum numbers from (3.1) are well defined. The total angular momentum of the molecule (without nuclear spins) in a state $|\Lambda, \Sigma, \Omega\rangle$ is given by

$$j = N + \langle j_e n \rangle n = N + (\Lambda + \Sigma)n = N + \Omega n \tag{3.2}$$

where N is the rotational angular momentum of the molecule as a whole.

Case b. The spin–rotation interaction dominates. In this case the projection Σ is not defined, but there are two additional quantum numbers S and K:

$$j = N + \Lambda n + S \equiv K + S. \tag{3.3}$$

For the heavy molecules this case takes place only if $\Lambda = 0$.

Case c. The spin–orbit interaction dominates. The only difference from the case a is the absence of the quantum numbers Λ and Σ.

Electronic states which differ by the signs of the quantum numbers Λ, Σ and Ω are degenerate. Because of the large energy difference between the non-degenerate electronic states, we will only be interested in the selection rules for the weak interaction operators within the degenerate subspace.

3.2. Selection rules for coupling case c

It is convenient to start from Hund's case c. If $|\Omega| \neq 0$ there are two degenerate states $|\Omega\rangle$ and $|-\Omega\rangle$. The most obvious selection rules can be found by irreducible tensor analysis. For electronic scalars, such as V_1^P, $\Delta\Omega = 0$. For electronic vectors, such as V_2^P, $\Delta\Omega = 0, \pm 1$.

Other selection rules correspond to the behaviour of the operators under spatial reflections and time reversal. It is seen from (3.1) that Λ, Σ and Ω change sign under both time reversal and spatial inversion (or reflection in any plane in the molecular frame of reference). Thus

$$P|\Omega\rangle \sim |-\Omega\rangle \qquad T|\Omega\rangle \sim |-\Omega\rangle. \tag{3.4}$$

It follows then, that the operator V_1^P does not have diagonal matrix elements. Indeed,

$$\langle\Omega|V_1^P|\Omega\rangle \stackrel{P}{=} \langle-\Omega|-V_1^P|-\Omega\rangle \stackrel{T}{=} -\langle\Omega|V_1^P|\Omega\rangle = 0. \tag{3.5}$$

Here we take into account that spatial inversion P changes the sign of the operator V_1^P, while time reversal T does not. Since $\Delta\Omega = 0$ for V_1^P, we conclude that this operator does not have non-zero matrix elements in the subspace of states $|\Omega\rangle$ and $|-\Omega\rangle$.

In order to obtain selection rules for the operator V_2^P, we shall apply symmetry operations to its electronic part, which is a T-odd polar vector. By applying the reflection operation in the plane passing through the molecular axis σ_v and time reversal T we have again

$$\langle\Omega|V_2^P|\Omega\rangle \stackrel{\sigma_v}{=} \langle-\Omega|V_2^P|-\Omega\rangle \stackrel{T}{=} -\langle\Omega|V_2^P|\Omega\rangle = 0. \tag{3.6}$$

But operator V_2^P, in contrast with operator V_1^P, has non-diagonal matrix elements:

$$\langle\Omega|V_2^P|-\Omega\rangle \neq 0 \qquad |\Omega| = \tfrac{1}{2}. \tag{3.7}$$

Taking into account that operator $V_1^{P,T}$ is an electronic P, T-odd scalar and operator $V_2^{P,T}$ is an electronic T-even polar vector one can easily show that (Sushkov and Flambaum 1978, Gorshkov *et al* 1979):

$$\langle\Omega|V_1^{P,T}|\Omega\rangle \neq 0, \Omega \neq 0 \qquad \langle\Omega|V_1^{P,T}|-\Omega\rangle = 0 \tag{3.8a}$$

$$\langle\Omega|V_2^{P,T}|\Omega\rangle \neq 0 \qquad \langle\Omega|V_2^{P,T}|-\Omega\rangle = 0, \Omega \neq 0. \tag{3.8b}$$

Selection rules for the operators V^d and V^S are the same as (3.8a) and (3.8b), respectively.

Similar analysis for the operator V^M shows that it also has non-zero matrix elements in the subspace of states $|\Omega\rangle$ and $|-\Omega\rangle$ provided that $\Omega \neq 0$ (Sushkov *et al* 1984). This last requirement is natural since the operator V^M describes the interaction of magnetic quadrupole moment of the nucleus with the electronic magnetic field.

Selection rules obtained in this section are summarized in table 1, where the signs '$-$' and '$+$' denote zero and non-zero matrix elements, respectively.

Table 1. Selection rules for operators of weak interactions. Signs '$-$' and '$+$' denote zero and non-zero matrix elements, respectively.

State	V_1^P	V_2^P	$V_1^{P,T}, V^S$	$V_2^{P,T}, V^d$	V^M
$\Omega = 0$	$-$	$-$	$+$	$-$	$-$
$|\Omega| = \tfrac{1}{2}$	$-$	$+$	$+$	$+$	$+$
$|\Omega| > \tfrac{1}{2}$	$-$	$-$	$+$	$+$	$+$

3.3. Selection rules for the coupling case a

Above we formulated selection rules for Hund's case c. Now we shall show that they can be applied to case a as well. It would appear that the existence of the quantum numbers Λ and Σ would result in additional selection rules for the PNC operators. Actually this is not so. Indeed, matrix elements of these operators depend mainly on the electronic wavefunction in the vicinity of the heaviest nucleus where relativistic effects are not small. Thus

the non-relativistic coupling described by the quantum numbers Λ and Σ is not valid here (Kozlov 1985).

For example, consider the simple single-electron wavefunction with quantum numbers $\Lambda = 0$, $\Sigma = \Omega = \frac{1}{2}$:

$$|0, \tfrac{1}{2}, \tfrac{1}{2}\rangle = a|s\rangle|\tfrac{1}{2}\rangle + b|p_0\rangle|\tfrac{1}{2}\rangle \tag{3.9}$$

where $|s\rangle$ and $|p_0\rangle$ are atomic orbitals and $|\tfrac{1}{2}\rangle$ is a spin function. One can make the transformation in (3.9) from the l, m_l, s, m_s representation to the l, s, j, m_j representation:

$$|0, \tfrac{1}{2}, \tfrac{1}{2}\rangle = a|s_{1/2}, \tfrac{1}{2}\rangle + b\left(-\frac{1}{\sqrt{3}}|p_{1/2}, \tfrac{1}{2}\rangle + \sqrt{\frac{2}{3}}|p_{3/2}, \tfrac{1}{2}\rangle\right). \tag{3.10}$$

Equations (3.9) and (3.10) are identical if the radial parts of the atomic orbitals satisfy the conditions: $R_s = R_{s_{1/2}}$ and $R_p = R_{p_{1/2}} = R_{p_{3/2}}$. This is approximately true for the large distances, but according to (2.5), in the vicinity of the Coulomb centre $R_{p_{1/2}} \gg R_{p_{3/2}}$ and the latter can be omitted:

$$|0, \tfrac{1}{2}, \tfrac{1}{2}\rangle \xrightarrow{r \to 0} a|s_{1/2}, \tfrac{1}{2}\rangle - \frac{b}{\sqrt{3}}|p_{1/2}, \tfrac{1}{2}\rangle. \tag{3.11}$$

It is now clearly seen that the right-hand side of this equation does not have quantum numbers Λ and Σ even approximately. It then follows that the selection rules for this function will correspond to Hund's case c.

3.4. Selection rules for the coupling case b

Hund's case b differs more significantly from cases a and c. But, for the most interesting particular case $\Lambda = 0$ and $S = \frac{1}{2}$ there is a simple connection between them. Transition to case b corresponds simply to the change of the quantization axis for the electron spin. It only results in the mixing of the diagonal and non-diagonal matrix elements of the PNC operators within the same degenerate subspace and thus does not influence the selection rules presented in table 1 for $|\Omega| = \frac{1}{2}$. This mixing can easily be treated in terms of the effective electron spin S' and spin–rotational Hamiltonian H_{sr} which are introduced in section 4.

4. Spin–rotational Hamiltonian

4.1. Effective spin

The spin–rotational Hamiltonian H_{sr} provides a convenient description of the spin–rotational degrees of freedom of a molecule in a particular electron vibrational state. In the first approximation it can be obtained by averaging of the molecular Hamiltonian over the electronic and vibrational wavefunctions. High-order terms of the adiabatic perturbation theory can be included as well. In this approach parameters of the operator H_{sr} are defined in terms of the electron vibrational matrix elements. On the other hand, these parameters can be determined from experiment by the analysis of the spin–rotational spectrum. It allows us to use the method of the spin–rotational Hamiltonian without complicated electronic calculations.

If a molecular electronic state is two-fold degenerate ($\Omega \neq 0$), a corresponding electronic degree of freedom must be included in the Hamiltonian H_{sr}. For the case of $|\Omega| = \frac{1}{2}$ it is convenient to define an effective spin S' by the following equalities:

$$S'_\zeta|\Omega\rangle = \Omega|\Omega\rangle \qquad S'_\pm|\Omega = \mp\tfrac{1}{2}\rangle = |\Omega = \pm\tfrac{1}{2}\rangle \qquad S'_\pm = S'_\xi \pm S'_\eta \tag{4.1}$$

where ξ, η and ζ form the molecular frame of reference with the ζ-axis directed along the vector n. From equation (4.1) it is seen that $S' = \frac{1}{2}$. In Hund's case b for $\Lambda = 0$, S' is equal to S.

Apart from the operator of effective spin, in the expression for H_{sr} operators n, J and nuclear spins I_1, I_2 can enter. The advantage of the definition of the spin-rotational Hamiltonian in terms of these operators is that their matrix elements are well known (see Landau and Lifshitz 1977) and thus calculation of the spin-rotational spectrum is easy.

4.2. Electronic state $\Omega = 0$

The spin-rotational Hamiltonian for this case was introduced by Boeckh *et al* (1964) who carried out a beam experiment on the TIF molecule. It looks as follows:

$$H_{sr}^0 = BJ^2 + c_1 I_1 J + c_2 I_2 J + c_3 I_1 \hat{R} I_2 + c_4 I_1 I_2 - Dn\mathcal{E} + (\mu_J J + \mu_1 I_1 + \mu_2 I_2)\mathcal{B} \tag{4.2}$$

$$R_{i,k} = n_i n_k - \frac{1}{3}\delta_{i,k}. \tag{4.3}$$

In equation (4.2) $\mathcal{E}$ and $\mathcal{B}$ are external electric and magnetic fields. Interaction between nuclear spins I_1 and I_2 is divided into tensor and scalar parts. For the TIF molecule parameters of this Hamiltonian are given in table 2. Note that $B \gg c_1 \gg |c_{2,3,4}|$. Stark and Zeeman terms become comparable with B and c_1 in the fields $\mathcal{E} \sim 10^3$ V cm^{-1} and $\mathcal{B} \sim 10^2$ Gs, respectively. For the TIF molecule both nuclei have spin-$\frac{1}{2}$ and the dimension of the subspace corresponding to the particular quantum number J is equal to $(2I_1 + 1)(2I_2 + 1)(2J + 1) = 4(2J + 1)$.

Table 2. Constants of the spin-rotational Hamiltonian for the TIF molecule.

Constants	B	c_1	c_2	c_3	c_4	D	μ_J	μ_1[a]	μ_2
Units[b]	(GHz)	(kHz)	(kHz)	(kHz)	(kHz)	(MHz V^{-1} cm^{-1})	(Hz Gs^{-1})	(kHz Gs^{-1})	(kHz Gs^{-1}))
Values	6.689 92	126.03	17.89	0.70	−13.30	2.1286	35	1.2405	2.003 63
								1.2285	

[a] Numbers are given for ^{205}Tl and ^{203}Tl, respectively.
[b] Frequency units for energy are used.

As was shown in section 3, only two operators $V_2^{P,T}$ and V^S have non-zero spin-rotational matrix elements. Corresponding terms in the spin-rotational Hamiltonian have the form (Coveney and Sandars 1983):

$$H_{sr}^{P,T} = (W_2^{P,T} g_2 + W^S S)I_1 n. \tag{4.4}$$

The expression in the right-hand side of (4.4) is obviously P, T-odd. Generally speaking there are also similar terms $\sim I_2 n$, but as far as $Z_{Tl} \gg Z_F$ and both constants $W \sim Z^2$, they can be neglected. The Hamiltonian

$$H_{sr} = H_{sr}^0 + H_{sr}^{P,T} \tag{4.5}$$

provides a complete description of the behaviour of the diamagnetic molecule in the ground electron vibrational state in the external electric and magnetic fields. As parameters of H_{sr}^0 are known from the experiment, the only theoretical problem is to calculate constants $W_2^{P,T}$ and W^S. This calculation appears to be rather difficult and is discussed in section 6 in some detail.

4.3. Electronic state $\Omega = \frac{1}{2}$

Almost all paramagnetic molecules which were discussed in the literature in connection with the PNC interactions have either $^2\Sigma_{1/2}$ or $^2\Pi_{1/2}$ ground states, i.e. $|\Lambda| = 0, 1$ and $|\Omega| = \frac{1}{2}$.

The presence of the non-zero effective spin results in a number of new large terms in the operator H_{sr}^0. Angular momentum J now includes rotational angular momentum of the molecule as a whole N and electronic angular momentum J_e (see equation (3.2)). Rotational energy is equal to

$$H_r = BN^2 = B(J - J_e)^2 = BJ^2 - 2BJJ_e + BJ_e^2. \tag{4.6}$$

Up to the term independent in J this expression can be written with the help of effective spin (Kozlov *et al* 1991)

$$H_r = BJ^2 + \Delta S'J \tag{4.7}$$

where Δ is the Ω-doubling constant

$$\Delta = 2B\langle \Omega = \tfrac{1}{2} | J_{e,\xi} + J_{e,\eta} | \Omega = -\tfrac{1}{2}\rangle. \tag{4.8}$$

It should be mentioned that (4.7) can be used not only in Hund's cases a and c, but in case b ($\Lambda = 0$) as well. For the latter transition to the standard notation is done by the substitutions

$$J = N + S \qquad \Delta = -2B + \gamma \tag{4.9}$$

where γ is the spin-doubling constant.

Apart from the second term in (4.7) there are three new terms which describe hyperfine interactions of the effective spin with two nuclei and with external magnetic field while the interaction with the external electric field remains unchanged:

$$H_{sr}^0 = BJ^2 + \Delta S'J + I_1\hat{A}_1 S' + I_2\hat{A}_2 S' - Dn\mathcal{E} + \mu_0 S'\hat{G}B + \cdots \tag{4.10}$$

where μ_0 is the Bohr magneton. Due to the molecular symmetry, all tensors in this formula are axial and have two independent components each. Dots stand for the terms similar to those in (4.2). As they correspond to the interactions of nuclear spins with each other and with the external field B, they are much smaller than terms explicitly written in (4.10) and usually can be neglected.

According to table 1 there are several new P-odd and P, T-odd terms here as well. Operators $V_1^{P,T}$ and V^d produce expression similar to (4.4) with substitution of S' instead of I_1:

$$(W_1^{P,T}g_1 + W^d d_e)S'n. \tag{4.11}$$

Interaction V^M is described by the tensor term (Sushkov *et al* 1984)

$$\frac{-W^M \mathcal{M}_1}{2I_1(2I_1 - 1)} S'\hat{T}_1 n \tag{4.12}$$

where the nuclear tensor $\hat{T}_1$ and the constant $\mathcal{M}_1$ are defined by (2.18)–(2.20). Again we are omitting interactions on the second nucleus similar to (4.11) and (4.12) assuming that $Z_1 \gg Z_2$. Note that expression (4.12) differs from zero only for $I_1 \geqslant 1$. In this case the interaction of the electric quadrupole moment of the first nucleus $\mathcal{Q}_1$ with the molecular electric field has to be added to (4.10) (Azuma *et al* 1990):

$$\frac{-q_0\mathcal{Q}_1}{8I_1(2I_1 - 1)} n\hat{T}_1 n. \tag{4.13}$$

There is also a P-odd term corresponding to operator V_2^P. Flambaum and Khriplovich (1985) showed that it can be written as follows:

$$W_2^P g_2^P n \times S' I_1 . \tag{4.14}$$

Combining together (4.10)–(4.14) we obtain the final expression for the spin–rotational Hamiltonian for the molecule in the electronic state $|\Omega| = \frac{1}{2}$:

$$H_{sr}^0 + H_{sr}^P + H_{sr}^{P,T} = BJ^2 + \Delta S'J + I_1\hat{A}_1 S' + I_2\hat{A}_2 S' - \frac{q_0 \mathcal{Q}_1}{8 I_1(2I_1 - 1)} n\hat{T}_1 n - Dn\mathcal{E}$$

$$+\mu_0 S'\hat{G}B + W_2^P g_2^P n \times S' I_1 + (W_1^{P,T} g_1 + W^d d_e)S'n$$

$$-\frac{W^M \mathcal{M}_1}{2I_1(2I_1 - 1)} S'\hat{T}_1 n . \tag{4.15}$$

This spin–rotational Hamiltonian includes a relatively small number of electronic parameters and describes the spin–rotational spectrum of the molecule. In particular, it describes transition from Hund's case c ($|\Delta| \ll B$) to the Hund's case b ($|\Delta + 2B| = |\gamma| \ll B$). It also describes more exotic cases. For example, if ($|A_{1,\|} - A_{1,\perp}| \gg B$), then for the lower rotational states nuclear spin I_1 is quantized on the molecular axis together with the effective spin S'. This case can take place for a molecule such as PbI, with two heavy nuclei (and thus very small B) and strongly anisotropic tensor $\hat{A}_1$.

Experimental values for the constants of the spin–rotational Hamiltonian for several molecules with ground state $^2\Sigma_{1/2}$ are given in table 3. For molecules MF, M = Ba, Yb, Hg or Pb the following relations take place:

$$B \sim |A_{1,\|}| \sim |A_{1,\perp}| \gg |A_{2,\|}| \sim |A_{2,\perp}| . \tag{4.16}$$

For this reason, for heavy metal isotopes with non-zero spin the lower part of the spin–rotational spectrum differs greatly from the pure rotational one due to the hyperfine interaction with the spin I_1. For the spinless metal isotopes spectrum it is mostly rotational with Ω-doubling for $^2\Pi_{1/2}$ states and γ-doubling for $^2\Sigma_{1/2}$ states. If one of the nuclear spins is equal to zero and the second one is equal to $\frac{1}{2}$, there is an analytic solution for the eigenvalue problem for operator $H_{s,r}^0$ in the absence of the external fields (Kozlov *et al* 1987).

Table 3. Constants of the spin–rotational Hamiltonians for paramagnetic molecules.

Molecule	B	γ[b]	$A_{1\|}$	$A_{1\perp}$	$A_{2\|}$	$A_{2\perp}$[c]	$G_\|$	$G_\perp$
^{137}BaF[d][e]	6471	83.3	2376	2301	67	59	2.0010	1.9950
^{137}BaF[f]	6480	81.03	2453	2401	—	—	—	—
^{171}YbF[d][g]	7237	—	7822	7513	220	134	1.9975	1.9954
^{199}HgF[h]	—	—	22621	21880	—	—	1.993	1.961
^{201}HgF[h]	—	—	−8054	−7760	—	—	1.993	1.961

(header: Constants[a])

[a] All constants with the exception for G-factors are in MHz.
[b] For connection with Δ see (4.9).
[c] The sign of this constant is unknown.
[d] Huber and Herzberg (1979).
[e] Knight *et al* (1971).
[f] Rizlewicz *et al* (1982).
[g] Van Zee *et al* (1978).
[h] Knight *et al* (1981).

5. PNC experiments with diatomics

The list of molecules which were mentioned in the literature in connection with the PNC experiments is rather long. In this section we shall name some of them and formulate several requirements for the molecules to be used in PNC experiments. We shall also give a brief description of the possible PNC experiments.

Since the pioneering works of Sandars (1965) and Bouchiat and Bouchiat (1974) it is known that atomic matrix elements of the weak interactions depend strongly on the nuclear charge Z: $\langle V_2^P \rangle$, $\langle V_2^{P,T} \rangle$, $\langle V^S \rangle$, $\langle V^M \rangle \sim Z^2$; $\langle V_1^P \rangle$, $\langle V_1^{P,T} \rangle$, $\langle V^d \rangle \sim Z^3$ (see sections 2 and 6 of this review). It is clear that the same Z dependence must take place for the electronic matrix elements of the PNC operators in molecules. For this reason almost all molecules which were proposed for PNC experiments include atoms with $Z > 50$. The search for P, T-odd effects requires the molecule to be polarized in an external electric field, thus favouring polar molecules.

These two requirements are met by molecules of the MX-type where M is a heavy metal and X is a halogen, oxygen, or sulphur.

5.1. Experiments for measuring the Schiff moment and the constant $g_2^{P,T}$

According to the selection rules from table 1, these measurements can be carried out with $\Omega = 0$ states. This allows the use of chemically stable diamagnetic molecules in the ground state. The technique of molecular beam spin resonance with two separated oscillating fields provides a very high accuracy for the measurements (Ramsay 1963). Sandars (1967) suggested the TlF molecule as the best candidate for this experiment. This molecule meets both requirements formulated above; it is relatively easy to produce and detect and has a simple spin–rotational spectrum since both nuclei are spin-$\frac{1}{2}$.

There is only one argument against the use of the TlF molecule (Khriplovich 1991) resulting from nuclear physics. Both stable isotopes of the Tl nucleus have one unpaired proton in the state $3s_{1/2}$. Then, equation (2.16) gives $\mathcal{S} = 0$, and within the shell-model contribution of the EDM of the proton to the Schiff moment of the nucleus is proportional to the difference $r_q^2 - r_d^2$. But $r_q \approx r_d$ and it is difficult to make a reliable estimate of this difference. This results in a large uncertainty in the interpretation of the TlF experiment in terms of the EDM of the proton in addition to the uncertainty of the molecular calculations.

This problem is absent for nuclei with a valence proton in any state different from $ns_{1/2}$. From this point of view it can be better to work with the CsF molecule. Molecular beams of CsF have been produced and its polarizability was measured (see Huber and Herzberg 1979). The disadvantages of this molecule are the lower Z of Cs in comparison with Tl and the more complicated spin–rotational spectrum (because of $I = \frac{7}{2}$) resulting in a lower population of a given level. Also, accurate molecular calculations for CsF can be even more difficult than for TlF.

5.2. Experiments for measuring constants $g_1^{P,T}$, d_e and $\mathcal{M}$ in the ground state

For these experiments one needs to use $\Omega \neq 0$ states. With very few exceptions $\Omega \neq 0$ ground states take place only for molecules with odd numbers of electrons. In this case usually $|\Omega| = \frac{1}{2}$ and $\Lambda = 0$ ($^2\Sigma_{1/2}$ states) or $|\Lambda| = 1$ ($^2\Pi_{1/2}$ states). In the single-particle approximation all but one electron are coupled and the single uncoupled electron occupies either a $\sigma_{1/2}$ or $\pi_{1/2}$ orbital. These molecules are chemical radicals and are stable only in a beam. Experiments of the same type as for the TlF molecule were proposed for PbF ($^2\Pi_{1/2}$),

HgF ($^2\Sigma_{1/2}$) and YbF ($^2\Sigma_{1/2}$) molecules (Varentsov *et al* 1985, 1986, Sauer *et al* 1994).

Atomic matrix elements of the PNC interactions decrease rapidly with the growth of the quantum numbers l and j. For the contact operators $V_{1,2}^{P,T}$ all matrix elements other than $\langle s_{1/2}|V|p_{1/2}\rangle$ are zero. The expansion of the $\sigma_{1/2}$ orbital over the atomic basis set includes both $s_{1/2}$ and $p_{1/2}$ terms, while expansion for the $\pi_{1/2}$ orbital starts from the $p_{1/2}$ term. That is why the matrix elements of the contact operators for the $^2\Pi_{1/2}$ state are proportional to the spin–orbital mixing of $\sigma_{1/2}$ and $\pi_{1/2}$ orbitals. So, we can expect larger PNC effects for the $^2\Sigma_{1/2}$ state.

The case $|\Omega| > \frac{1}{2}$ deserves special consideration. According to the selection rules the matrix elements of operators $V_l^{P,T}$, V^d and $V^{\mathcal{M}}$ are not zero but they are strongly suppressed. On the other hand, polarizability of these molecules in the low-field limit is very high due to the extremely small Ω-doubling (splitting of levels with opposite parity). As a result, molecular Stark shifts calculated with the help of (2.9), (2.12b) and (2.23) will be larger than for the case $|\Omega| = \frac{1}{2}$. This argument can be found in the literature but, from our point of view, is misleading. In contrast with the atoms, where the low-field limit (when these equations are valid) can be used for all external fields available in laboratory conditions, heavy polar molecules can be completely polarized in the field $\sim 10^4$ V cm^{-1} even if $|\Omega| = \frac{1}{2}$. This means that the levels of opposite parity are completely mixed by the external field and the P, T-odd effects are determined solely by the electronic matrix elements of the P, T-odd operators which are maximal for the $|\Omega| = \frac{1}{2}$ states.

High polarizability can be found not only for molecules with $|\Omega| > \frac{1}{2}$ but also for those with two heavy atoms, such as MBr or MI. There is no suppression of the electronic matrix elements here and one can expect the same P, T-odd effects in the lower fields. But, as we saw in section 4, the lower part of the rotational spectrum is strongly influenced by the hyperfine interaction and the spacing between levels of the opposite parity can be changed significantly. There can even be some new selection rules for these molecules due to the quantization of the nuclear spin on the molecular axis. On the other hand, all stable isotopes of the heavy halogens have nuclear spin $I \geqslant \frac{3}{2}$. This, together with a small rotational constant, results in a large statistical sum and thus the low population of a given level. As a result, it is hardly useful to make the PNC experiments on the molecules with heavy halogens.

5.3. Experiments for measuring constants $g_1^{P,T}$, d_e and $\mathcal{M}$ in optical transitions

From the experimental point of view, it is much easier to work with the chemically stable molecules than with radicals. This also makes it possible to do experiments in a cell instead of a beam. That is why, the idea of Sushkov and Flambaum (1978) to observe the Faraday rotation in an external electric field looks very attractive. One needs a $|\Omega = 0\rangle \longrightarrow |\Omega = \pm 1\rangle$ transition to observe this effect and it is sufficient here to have PNC mixing of the levels of opposite parity in the excited electronic state. The second important step was made by Barkov *et al* (1988) who realized that the sensitivity of this experiment can be increased by three orders of magnitude if one can saturate the corresponding transition. Actually it is the direct analogue of the well known nonlinear Faraday effect.

Flambaum (1987) and Barkov *et al* (1988) suggested looking for this effect in the $^1\Sigma_0 \longrightarrow {}^3\Sigma_1$ (16 025 cm^{-1}) transition of the PbO molecule. The excited state $|\Omega| = 1$ has two unpaired electrons and there is no suppression of the PNC matrix elements if at least one of them occupies the $\sigma_{1/2}$ orbital. However, in the PbO molecule it is more likely that unpaired electrons occupy two different π orbitals. As a result, one can expect approximately one order of magnitude suppression of the PNC effects.

5.4. Experiments for measuring the constant g_2^P

There is particular interest in measuring the constant g_2^P in the hydrogen molecule where it is directly associated with the proton. Corresponding optical experiments were suggested by Neronov and Barzakh (1978) and Gorshkov *et al* (1978). More detailed calculations were made by Kopp (1983) for the mixing of $^3\Sigma_g^+$ (*para*) and $^3\Pi_u^-$ (*ortho*) metastable states of the hydrogen molecule by the interaction V_2^P. Unfortunately, for the hydrogen molecule the constant W_2^P is of the order of 10^{-3} Hz and all these experiments are extremely difficult.

P-odd effects in the heavy molecules are caused by the anapole moment of the nucleus. As we shall see below constant W_2^P can reach the order of 10^3 Hz for PbF and YbF molecules and even more for HgF. The P-odd correlation $(n \times S'I)$ can be seen in the beam experiment similar to the EDM one. This correlation is more complicated than the P, T-odd correlation $(S'n)$ and can be observed only if the coupling of spins S' and I is broken, i.e. in the strong external field.

One can also look for parity non-conservation in the M1 transitions between spin-rotational levels. For experiments of this type it is convenient to introduce a parity non-conservation rate

$$\mathcal{P} = \left| \frac{A_{E1}^{PNC}}{A_{M1}} \right| = \left| \frac{A_{E1}\xi^P}{A_{M1}} \right|$$

where A_{E1}^{PNC} is the E1 transition amplitude induced by the P-odd interaction, A_{E1} and A_{M1} are the ordinary E1 and M1 transition amplitudes and ξ^P is the mixing coefficient of the states of opposite parity. It is natural to assume that $A_{E1} \sim D\mathcal{E}_0$, $A_{M1} \sim \mu_0 G_\perp \mathcal{B}_0$, where $\mathcal{E}_0$ and $\mathcal{B}_0$ are the amplitudes of the oscillating field (note that for the microwave experiments these amplitudes are not necessarily equal). The coefficient ξ^P is of the order of $W_2^P g_2^P / B$. Then

$$\mathcal{P} \sim \frac{W_2^P D\mathcal{E}_0}{B\mu_0 G_\perp \mathcal{B}_0} g_2^P \sim 10^{-4} g_2^P \;.$$

Numerical calculations proved that this estimate is close to the averaged $\mathcal{P}$ value for the spin–rotational spectrum of the PbF molecule but the individual values can differ very strongly (Kozlov 1988).

In principle, it is possible to achieve further enhancement of the P-odd effects by applying a constant magnetic field to cross the spin–rotational levels of opposite parity (Kozlov *et al* 1991). Let us look at this phenomenon in some detail.

Diagonalization of the spin–rotational Hamiltonian for PbF and HgF molecules shows that there are several crossings of the levels of opposite parity below 10^4 Gs. If projection of the total angular momentum on the external field for the crossing levels i and k is the same, the interaction V_2^P transforms these crossings to pseudocrossings with the splittings equal to $2|\langle i|V_2^P|k\rangle|$. Calculated values for the magnetic field and P-odd matrix elements at the crossing points are given in table 4. In these calculations where it is possible experimental values from table 3 are used for the parameters of the spin–rotational Hamiltonian. Parameter W_2^P as well as other not measured parameters of the operator H_{sr} are taken from the molecular calculations (see section 6 and table 7).

At the crossing points P-odd effects are determined by the ratio $W_2^P g_2^P / \Gamma$ rather than parameter $\mathcal{P}$, where Γ is the linewidth. So, for the E1 spin–rotational transition the line profile will be a double-hampered curve with the peak-to-peak distance equal to $2|\langle i|V_2^P|k\rangle|$. For the beam experiment $\Gamma = 1/\tau$, where τ is the time-of-flight and $2|\langle i|V_2^P|k\rangle|/\Gamma \sim W_2^P g_2^P / \Gamma$ can be of the order of unity. The main problems with this

Table 4. Matrix elements of the operator V_2^P at the pseudocrossings of the spin–rotational levels of opposite parity for PbF and HgF molecules in external magnetic field.

Molecule[a]	Crossing levels		B	$\dfrac{|\langle i|V_2^P|k\rangle|}{\delta_2^P}$
	i	k	(10^3 Gs)	(Hz)
PbF	$(\frac{3}{2}, 1, \frac{3}{2}, -\frac{3}{2}, +)$	$(\frac{3}{2}, 1, \frac{3}{2}, -\frac{3}{2}, -)$	9.78	360
HgF	$(1, \frac{1}{2}, 1, \frac{3}{2}, \frac{1}{2}, -)$	$(0, \frac{1}{2}, 2, \frac{3}{2}, \frac{1}{2}, +)$	2.23	110
HgF	$(1, \frac{1}{2}, 1, \frac{1}{2}, \frac{1}{2}, -)$	$(0, \frac{1}{2}, 2, \frac{5}{2}, \frac{1}{2}, +)$	2.99	90

[a] Parameters of the spin–rotational Hamiltonians are taken from tables 3 and 7.
[b] For PbF molecule levels are labelled by the quantum numbers: J, F_1, F, M_F and p, where $F_1 = J + I_1$, $F_2 = F_1 + I_2$ and p is parity. For HgF molecule levels are labelled by the quantum numbers: F_1, F_2, N, F, M_F and p, where $F_1 = S + I_1$, $F_2 = F_1 + I_2$ and $F = N + F_2$. For both molecules all quantum numbers other than M_F, and p are good only in the low-field limit.

experiment are associated with the stray electric and magnetic fields: while the former mimics the P-odd splitting, the latter moves the system from the crossing point.

6. Electronic calculations

6.1. TlF molecule

As we mentioned above both experimental and theoretical studies of the P, T-odd effects in diamagnetic diatomics were restricted to the TlF molecule. Here we are going to look at the main features of the method of calculation developed by Hinds and Sandars (1980a), henceforth referred to as HS.

The molecular part of the calculation is performed within the non-relativistic Hartree–Fock–Roothaan method in the basis set of Slater-type atomic orbitals (AOs). Operators V^S and $V_2^{P,T}$ are both of the contact type and only σ-type molecular orbitals (MOs) contribute to their matrix elements. At the nucleus σ MOs ($\lambda = 0$) can be expanded in spherical waves as

$$|\lambda = 0\rangle = \sum_{l=0}^{\infty} a_l r^l Y_m^l(\theta, \phi).$$ (6.1)

In the non-relativistic approximation matrix elements of V^S and $V_2^{P,T}$ are proportional to the sum over all electrons

$$X = \sum_i X_i = \frac{1}{\sqrt{3}} \sum_i a_0^i a_1^i.$$ (6.2)

Contributions of different MOs to this factor are listed in table 5 and summation gives (note that each MO is doubly occupied)

$$X = 741 \text{ au}.$$ (6.3)

This procedure ignores the fact that in the vicinity of the Tl nucleus electrons are highly relativistic. HS calculated a relativistic enhancement factor R to parameter X in two steps. First they derived a relativistic analogue of (6.2). Then for each MO they solved numerically the radial Dirac equation in the vicinity of the Tl nucleus for an energy equal to that of the MO. The resultant radial Dirac wavefunction was normalized by matching the large component with the non-relativistic radial function obtained by the spherical expansion of the MO. This matching was made at the antinode at approximately 0.1 au from the Tl nucleus

Table 5. Orbital contributions to the factor X for the TlF molecule and Xe atom. For TlF relativistic enhancement factors R_i obtained by the matching procedure of HS are given as well. For Xe the orbital mixing within the subspace of doubly occupied orbitals is excluded.

MO	TlF X_i (au)	R_i	AO	Xe $X_i/\mathcal{E}_0$ (au)
2σ	-277.1	—	2s	—
3σ	279.7	—	2p	—
4σ	-449.2	5.93	3s	-0.6
5σ	459.6	6.31	3p	-1.2
8σ	-678.3	3.42	4s	-3.6
9σ	698.4	3.41	4p	-1.5
11σ	-784.4	3.15	5s	-318.8
13σ	787.2	3.14	5p	-3084.2
14σ	-30.3	3.23	—	—
16σ	-265.9	3.15	—	—
17σ	631.0	3.11	—	—

where the molecular potential is still close to that of the atom and relativistic effects are already small (Sandars and Beck 1965). For the interaction V^S HS found

$$R = 3.15. \tag{6.4}$$

HS used the minimal basis set of the Slater-type orbitals. Later Coveney and Sandars (1983) repeated calculations using a double-zeta basis set. For the equilibrium internuclear distance they give

$$X = 294.5 \text{ au} \qquad R = 7.1 \tag{6.5}$$

and the corresponding parameters of the spin–rotational Hamiltonian are:

$$W^S = 2.2 \times 10^{37} \text{ MHz e}^{-1} \text{ cm}^{-3} \tag{6.6}$$

$$W_2^{P,T} = 3.7 \times 10^{-4} \text{ MHz}. \tag{6.7}$$

Analysis of Coveney and Sandars showed a strong dependence of the results on the internuclear distance and on Slater exponents ζ. They concluded that more reliable calculations need to be done.

Let us discuss the accuracy of these calculations in more detail. If a non-relativistic molecular calculation is made, there are two different problems to be solved, i.e. evaluation of X and evaluation of R. The first of them requires extensive molecular calculations while the second is actually an atomic problem. The last statement is based on two observations:

(i) The main contribution to X comes from the valence electrons (see below). Their orbital energies are ~ 1 au and at the matching distances can be neglected in comparison with the potential energy.

(ii) The relativistic factor depends on the potential in the vicinity of the heavy nucleus where it is close to Z/r.

It follows that the factor R only depends on the nuclear charge Z and can be calculated in the same way as for atoms (see Khriplovich 1991). The relativistic analogue of (6.1) is the expansion of the MO in four-component spherical waves:

$$|\lambda, \omega\rangle = \sum_{l,j=l\pm1/2} C_{l,j}|l, j, \omega\rangle \tag{6.8}$$

$$|l, j, \omega\rangle = \begin{pmatrix} f_{l,j} Y^l_{j,\omega} \\ ig_{l,j} Y^{l'}_{j,\omega} \end{pmatrix} \tag{6.9}$$

where f and g are radial functions, $Y^l_{j,\omega}$ is the spherical spinor, $l' = 2j - l$.

In the vicinity of the nucleus functions f and g can be found up to the normalization constant from the simple radial Dirac equation with zero energy and potential Z/r. Solutions of this equation are expressed in terms of Bessel functions:

$$\begin{pmatrix} f_{l,j} \\ g_{l,j} \end{pmatrix} = \frac{k}{|k|} \frac{a_l}{Z^{1/2}r} \begin{pmatrix} (\gamma_j + k)J_{2\gamma_j}(x) - \frac{1}{2}xJ_{2\gamma_j-1}(x) \\ \alpha Z J_{2\gamma_j}(x) \end{pmatrix} \tag{6.10}$$

where

$$x = \sqrt{8Zr} \qquad \gamma_j = \sqrt{(j+1/2)^2 - \alpha^2 Z^2} \qquad k = (l-j)(2j+1). \tag{6.11}$$

Normalization coefficients a_l are of the order of unity and with good accuracy are independent of j. They are determined by matching with the solution of the non-relativistic Schrödinger equation in the outer region.

It is well known that for $j = \frac{1}{2}$ expression (6.10) diverges at the origin. This leads to the infinite value for R. A standard trick is to evaluate all diverging expressions at $r = r_N$ rather than at $r = 0$ (r_N is the nuclear radius). The accuracy of this approximation is usually about 10–20%.

Not all coefficients $C_{l,j}$ in (6.8) are independent. Indeed, for each $l \neq 0$ a pair of functions with $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$ at large distances have to form the non-relativistic function $|l, m_l = \lambda, \omega)$. For example, for σ MOs the following relations hold true:

$$C_{1,3/2} = -\sqrt{2}C_{1,1/2} \qquad C_{2,5/2} = -\sqrt{3/2}C_{2,3/2} \quad \text{etc}. \tag{6.12}$$

Using these relations one can easily check that for the operator V^S the non-relativistic expression $\psi_s \psi'_p$ which leads to (6.2) must be substituted by $\psi_{s_{1/2}}(\psi'_{p_{1/2}} + 2\psi'_{p_{3/2}})/3$. It is easy to calculate this expression by expanding Bessel functions in (6.10) in a power series. Now one needs to single out the factor which turns to unity if $\alpha Z \to 0$. This is the relativistic enhancement factor to be found. Its explicit form appears to be $R = (R_{1/2} + 2R_{3/2})/3$, where

$$R_{1/2} = \frac{4(2Zr_N)^{2\gamma_{1/2}-2}}{\Gamma^2(2\gamma_{1/2} + 1)} \tag{6.13}$$

$$R_{3/2} = \frac{6[(\gamma_{1/2} + 1)(\gamma_{3/2} + 1) + (\alpha Z)^2](\gamma_{1/2} + \gamma_{3/2} - 2)(2Zr_N)^{\gamma_{1/2}+\gamma_{3/2}-3}}{\Gamma(2\gamma_{1/2} + 1)\Gamma(2\gamma_{3/2} + 1)}. \tag{6.14}$$

For $Z = 81$ these equations give $R = 5.2$†.

The difference of the values of the factor R given by HS (6.4) and by Coveney and Sandars (6.5) from that of Khriplovich suggests that non-relativistic orbitals obtained from a molecular calculation have improper behaviour at small distances from the nucleus. The matching procedure of HS tends to compensate for inaccuracy of the molecular wavefunction. But one can expect that for the more flexible molecular basis sets it will give values close to the atomic one. Note that the latter can easily be improved with the help of the wavefunctions for the finite nucleus.

The accurate calculation of the factor X is a more complicated problem. One needs to use extended basis sets to obtain a good wavefunction at the Tl nucleus. It is also necessary to check the accuracy of the wavefunction in this region. Two tests seem to be important. First is the value of the electric field at the nucleus. It must turn to zero in the Hartree–Fock limit but can differ from zero for the finite basis sets. The second is the value of the quadrupole constant q_0 (4.13). Unfortunately, the Tl nucleus does not have a nuclear quadrupole moment.

† In a similar way one can find that the enhancement factor for the operator $V^{P,T}_2$ is $R = R_{1/2}(2 + \gamma_{1/2})/3 = 7.9$.

The role of the core electrons in the calculations of X is not quite clear. It is seen from table 5 that there are large contributions of the core MOs as well as severe cancellations between them. This can be explained by the mixing of AOs of s- and p-type within the same shell. But as long as all of them are doubly occupied this mixing does not influence the final result. The important mixing occurs only between the occupied and unoccupied orbitals which is much smaller.

We examined this problem for the much simpler example of the Xe atom in the external electric field. We used Hartree–Fock perturbation theory in the basis set of HF atomic orbitals to calculate an atomic wavefunction in the external field $\mathcal{E}_0$. Perturbation theory was reformulated to exclude mixing of the occupied orbitals. We checked the electric field at the nucleus which appeared to be less than 3% of $\mathcal{E}_0$. Our results are listed in table 5. The sum over electrons gives

$$X/\mathcal{E}_0 = -3410 \text{ au}. \tag{6.15}$$

This value has to be compared with the results of the more extended calculations of Dzuba *et al* (1984) and Mårtensson-Pendrill (1985) who calculated the EDM of a Xe atom induced by the interaction $V_2^{P,T}$. Dividing their results by the relativistic factor $R = R_{1/2}\frac{2+\gamma_{1/2}}{3} = 2.65$ we obtain $X = -2550$ au and $X = -3234$ au, respectively, which is in reasonable agreement with (6.15).

From this example one can see that the net contribution of the inner shells to the screening of the external field and to the factor X is small. If it is true, in the molecular calculations it is possible to use the frozen-core approximation. As long as the molecular internal field is strong on the atomic scale it can be better to exclude the shell next to the valence one out of the core.

The influence of the core polarization on the factor X can be studied in the calculation of the CsF molecule where it must be more important. Indeed, the single valence electron of Cs is strongly attracted by the fluorine and its contribution to the screening as well as to the factor X and the constant q_0 must be relatively small.

If an all-electron calculation is performed it is still possible to use the single relativistic enhancement factor calculated for outer orbitals (neglecting the orbital energy in comparison with the potential energy). At least it is important to use equal relativistic enhancement factors for orbitals originating from one atomic shell to allow the compensation mentioned above to take place.

There are preliminary results of the new calculation for the TlF molecule (Williams *et al* 1994) with a much better basis set. The total energy of the molecule is approximately 20 Hartrees lower than in the calculation of Coveney and Sandars. There are also some perspectives on the relativistic calculation of this molecule.

6.2. Paramagnetic molecules—semi-empirical approach

In this section we describe semi-empirical calculations of BaF, YbF and HgF molecules. All of them have the ground state $^2\Sigma_{1/2}$ and are candidates for the EDM experiments. The method used here was developed by Kozlov (1985). It is based on the close connection between matrix elements of the PNC interactions with matrix elements of the magnetic hyperfine interaction. The hyperfine structure constants can be measured by means of the electron-spin resonance (see table 3), thus making it possible to reproduce electron-spin density in the vicinity of the nucleus.

The main features of all these polar molecules can be understood from the following model. One of the outermost 6s-electrons of the metal atom moves to fluorine and closes its

2p-shell. The M^+ ion remains with the unpaired electron on the orbit, strongly polarized by the F^- ion along the molecular axis. This single unpaired electron is of primary importance for our considerations. Indeed, coupled electrons do not contribute to the hyperfine constants as well as to the P-odd and P, T-odd constants of the spin–rotational Hamiltonian (4.15).

In the single-particle approximation the unpaired electron occupies MO with $\lambda = 0$ and $|\omega| = \frac{1}{2}$. At present we assume that λ is a good quantum number in the sense of (6.12). The accuracy of this assumption is discussed below.

In the vicinity of the nucleus of the heavy metal atom the wavefunction can be expanded in spherical waves according to (6.8)–(6.12). For small r only the first several terms of the series (6.8) are important. In this region the molecular wavefunction is determined by the products

$$\sigma_s = C_{0,1/2}a_0 \qquad \sigma_p = C_{1,1/2}a_1 \qquad \sigma_d = C_{2,3/2}a_2 \quad \text{etc} \qquad (6.16)$$

where coefficients a_l are from (6.10).

Using equation (6.10) we can now express matrix elements of all operators which depend mainly on the wavefunction of the unpaired electron in the vicinity of the heavy nucleus in terms of few first constants σ_i. Such operators must be (i) singular at the origin and (ii) depend on electron spin (a second feature is necessary to eliminate contributions of the coupled electrons).

The hyperfine tensor $\hat{A}$ has two independent parameters. It is convenient to use the following combinations of $A_\parallel$ and $A_\perp$:

$$A = \frac{A_\parallel + 2A_\perp}{3} \qquad A_d = \frac{A_\parallel - A_\perp}{3}. \qquad (6.17)$$

These parameters can be expressed in terms of the radial integrals for the hyperfine interaction operator as follows (Kozlov 1985):

$$A = \tfrac{4}{3}C_{-1}^2 h_{-1,-1} + \tfrac{4}{9}C_1^2 h_{1,1} - \tfrac{8\sqrt{2}}{9}C_1 C_{-2}h_{1,-2} + \tfrac{8}{9}C_{-2}^2 h_{-2,-2}$$
$$+ \tfrac{8}{15}C_2^2 h_{2,2} - \tfrac{8\sqrt{6}}{15}C_2 C_{-3}h_{2,-3} + \tfrac{4}{5}C_{-3}^2 h_{-3,-3} + \cdots \qquad (6.18)$$

$$A_d = -\tfrac{8}{9}C_1^2 h_{1,1} - \tfrac{2\sqrt{2}}{9}C_1 C_{-2}h_{1,-2} - \tfrac{8}{45}C_{-2}^2 h_{-2,-2}$$
$$- \tfrac{8}{15}C_2^2 h_{2,2} - \tfrac{2\sqrt{6}}{15}C_2 C_{-3}h_{2,-3} - \tfrac{8}{35}C_{-3}^2 h_{-3,-3} + \cdots \qquad (6.19)$$

$$h_{k,k'} = -\frac{g_n \alpha}{2m_p} \int_0^\infty (f_k g_{k'} + g_k f_{k'})\, dr \qquad (6.20)$$

where we used the single index k from (6.11) instead of l, j in (6.8), g_n is G-factor of the nucleus and m_p is the proton mass. For functions (6.10) these integrals are calculated analytically:

$$h_{k,k'} = -\frac{g_n \alpha}{m_p} \frac{2\,\text{sign}(kk')\alpha Z^2 a_l a_{l'}\sin(\pi(\gamma_j - \gamma_{j'}))(k' + k - 1)}{\pi(\gamma_j + \gamma_{j'})((\gamma_j + \gamma_{j'})^2 - 1)(\gamma_j - \gamma_{j'})(1 - (\gamma_j - \gamma_{j'})^2)}. \qquad (6.21)$$

Now with the help of experimental values for hyperfine constants from table 3 it is easy to obtain system of equations for parameters σ_i. For the YbF molecule this system looks as follows (Kozlov and Ezhov 1994):

$$31\,170\sigma_s^2 - 1330\sigma_p^2 - 50\sigma_d^2 + \cdots = 7617$$
$$5510\sigma_p^2 + 370\sigma_d^2 + \cdots = 102. \qquad (6.22)$$

It is seen that contributions of the spherical waves rapidly decrease as the orbital angular momentum increases. On this ground we can neglect contributions of the waves with $l \geqslant 2$. Then

$$\sigma_s^2 = 0.24 \qquad \sigma_p^2 = 0.019 . \tag{6.23}$$

More detailed analysis shows that the error from neglecting the d-wave must be less then 5% for σ_p^2 and even smaller for σ_s^2.

To calculate matrix elements of the P, T-odd operators we have to fix the sign of the product $\sigma_s \sigma_p$. Using the ionic model of the molecule one can easily see that interference of s- and p-waves has to be destructive on the inner side and constructive on the outer side of the metal ion. If phases are fixed so that $a_l > 0$ and the quantization axis is directed from the metal atom to F, then $\sigma_s \sigma_p < 0$.

Above we used (6.12) to reduce the number of independent variables in the system (6.22). These relations are valid for MOs with quantum number $\lambda = 0$. The spin–orbit interaction mixes MOs with the same ω but different λ. It also determines splittings of the sublevels with $\omega = \lambda \pm \frac{1}{2}$ of the state λ. The main admixture to the ground state can be expected from the first excited state Π ($\lambda = 1$) with energy $18\,000$ cm^{-1} (see Herzberg 1957). Comparison of the spin–orbital splitting of the substates $\Pi_{1/2}$ and $\Pi_{3/2}$ with that for the 6p state of Yb$^+$ shows that the 6p-orbital contributes about 60% to the π MO. The contribution of the 6p-orbital to the σ MO can be estimated as 23% using (6.23) and the semiclassical value for the parameter $a_l^2 \approx 0.23$. Then, spin–orbital mixing of these states is

$$\xi = \frac{\langle \lambda = 1, \omega | H_{so} | \lambda = 0, \omega \rangle}{E_0 - E_1}$$

$$= (0.6 \times 0.23)^{1/2} \frac{\langle 6p, \lambda = 1, \omega | H_{so} | 6p, \lambda = 0, \omega \rangle}{18\,000 \text{ cm}^{-1}} \approx -0.03 . \tag{6.24}$$

An alternative way to calculate ξ was used by Kozlov (1985) for BaF and HgF molecules. It can be readily shown that the spin–orbital mixing of $\Sigma_{1/2}$ and $\Pi_{1/2}$ states influence the $\hat{G}$ tensor so that

$$G_\perp - G_\parallel = 2\xi\sqrt{1 - \xi^2} \langle \lambda = 1 | l_+ | \lambda = 0 \rangle . \tag{6.25}$$

For the YbF molecule this method gives an even smaller value for ξ, but there is some uncertainty caused by the unknown contribution of the d-wave to the matrix element (ME) in (6.25). We conclude, that for the YbF molecule the accuracy of (6.12) is about 3% or better.

Spin–orbital mixing for the HgF molecule can be more important. Ignoring contributions of the waves $l \geqslant 2$ to the ME $\langle \lambda = 1 | l_+ | \lambda = 0 \rangle$ in (6.25) we can change (6.12) to account for the spin–orbital mixing:

$$C_{1,3/2} = -\sqrt{2}C_{1,1/2} - \frac{G_\perp - G_\parallel}{4C_{1,1/2}} . \tag{6.26}$$

Using experimental data from table 3 it is easy to calculate the product $\sigma_s \sigma_p$ for BaF and HgF. The usage of (6.26) instead of (6.12) leads to the 3% correction to this product for the HgF molecule.

With the help of (6.10) electronic matrix elements of the PNC operators are easily

expressed in terms of the constants σ_i. For example, $\langle \lambda, \omega | V^d | \lambda, \omega \rangle = W^d d_e \omega$ and

$$W^d = 8 \sum_i C_{-i} C_i \int_0^\infty g_{-i} g_i \frac{d\phi}{dr} r^2 \, dr$$

$$= 16\alpha^2 Z^3 \left(\frac{\sigma_s \sigma_p}{\gamma_{1/2}(4\gamma_{1/2}^2 - 1)} - \frac{\sqrt{2}\sigma_p \sigma_d}{\gamma_{3/2}(4\gamma_{3/2}^2 - 1)} + \cdots \right) \tag{6.27}$$

where γ_j is defined in (6.11). For YbF this equation gives $W^d = 174\sigma_s \sigma_p - 15\sigma_p \sigma_d + \cdots$. It is again seen that contributions of the waves with $l > 1$ are strongly suppressed.

Other constants of the spin–rotational Hamiltonian are calculated in a similar way. Numerical values are given in table 6.

Table 6. Results of the semi-empirical calculations for BaF, YbF and HgF molecules.

Molecule	$\sigma_s \sigma_p$	W^d $(10^{25}$ Hz e^{-1} cm$^{-1})$	$W_1^{P,T}$ $(10^3$ Hz$)$	W_2^P (Hz)	W^M $(10^{33}$ Hz e^{-1} cm$^{-2})$
BaF[a]	−0.050	−0.35	−11	210	−0.83
BaF[b]	−0.057	−0.41	−13	240	−0.98
YbF[c]	−0.067	−1.5	−48	730	−2.1
HgF[d]	−0.12	−4.7	−203	2700	−4.8

Experimental data for the hyperfine constants are taken from:
[a] Knight *et al* (1971).
[b] Rizlewicz *et al* (1982).
[c] Van Zee *et al* (1978).
[d] Knight *et al* (1981).

6.3. Paramagnetic molecules—ab initio calculations

The main difficulties in the calculation of PNC effects in paramagnetic diatomics are the same as for the closed-shell diatomics: (i) a large number of the electrons and (ii) a necessity for the correct description of the electron wavefunction at the heavy nucleus.

On the other hand here we are interested in the electron-spin-dependent PNC interactions. For this reason the contribution of the core electrons is strongly suppressed and can be ignored. This makes possible the use of the relativistic effective core potential (RECP) approach (see reviews by Balasubramanian and Pitzer 1987 and Ermler *et al* 1988). Up to now the only *ab initio* calculations of the PNC effects in diatomic radicals PbF and HgF were done within this approach (Dmitriev *et al* 1985, 1986, 1992, Kozlov *et al* 1987).

RECP helps to solve the first problem mentioned and to diminish the number of electrons involved essentially in the numerical calculations. The second problem can be solved by the procedure proposed in the works cited above. This procedure is incorporated as a last step in the algorithm for the numerical calculations of the PNC effects in the open shell diatomics. The total algorithm consists of five steps.

First step: atomic SCF calculation. Population analysis as well as the large value of the dipole moment of both molecules show that the metal atom is positively charged. For this reason atomic calculations were done for the M^+ ions with the help of the Hartree–Fock–Dirac program developed by Bratsev *et al* (1977).

Second step: construction of the RECP. Chemical bonds are formed in the space region where the valence electrons can be considered as non-relativistic even for heavy atoms. Then it is natural to consider the inner shells of the relativistic electrons as a frozen core and to introduce the RECP (Kahn 1984). In this approach the valence atomic orbitals ϕ_{nlj}^v are replaced by the pseudo-orbitals Φ_{nlj}^v which coincide with the true ones outside the core region and are smoothed inside this region. Following Christiansen *et al* (1979) the large components of the pseudo-orbitals are written as

$$
F_{nlj}^v = \begin{cases} \sum_i C_i r^i & r < r_m \\ f_{nlj}^v & r > r_m \end{cases} \tag{6.28}
$$

where f_{nlj}^v is the large component of the orbital ϕ_{nlj}^v and r_m is a matching radius. Coefficients C_i are determined by matching the value and the first three derivatives of F_{nlj}^v and f_{nlj}^v at r_m with the normalization condition for F_{nlj}^v. The matching radius is minimized subject to the condition that F_{nlj}^v can have only one antinode and two inflection points. Pseudo-orbitals of this type are called shape-consistent (Kahn *et al* 1976).

For the nodeless pseudo-orbitals F_{nlj}^v the RECP can be defined as (Wadt and Hay 1985)

$$
U^{\text{RECP}}(r) = U_{LJ}^{\text{RECP}}(r) + \sum_{l=0}^{L-1} \sum_{j=l\pm1} \sum_{m=-j}^{j} (U_{lj}^{\text{RECP}}(r) - U_{LJ}^{\text{RECP}}(r))|ljm\rangle\langle ljm| \tag{6.29}
$$

where the radial RECP U_{lj}^{RECP} is obtained from the Schrödinger-like equation

$$
U_{lj}^{\text{RECP}} = \frac{1}{F_{nlj}^v}\left(\epsilon_{nlj} + \frac{1}{2}\frac{d^2}{dr^2} - \frac{1}{2}\frac{k(k+1)}{r^2} - \hat{W}_{nlj}\right)F_{nlj}^v \tag{6.30}
$$

where ϵ_{nlj} is the orbital energy, $\hat{W}_{nlj}$ is the sum of the Coulomb and exchange operators, k is defined in (6.11), $|ljm\rangle$ is the angular Pauli spinor. The maximum value of l in the expansion (6.29) denoted by L is usually chosen as $L = l_{occ}^{max} + 1$ where l_{occ}^{max} is the maximum l for the occupied orbitals. For PbF and HgF molecules $l_{occ}^{max} = 3$.

Third step: molecular SCF calculation. For the non-relativistic molecular SCF calculation RECP should be averaged over the quantum number j:

$$
U_l^{\text{ARECP}} = \frac{1}{2l+1}\left(l U_{l,l-1/2}^{\text{RECP}} + (l+1)U_{l,l+1/2}^{\text{RECP}}\right). \tag{6.31}
$$

Molecular SCF calculations were made with this potential to obtain the two lower molecular states $^2\Sigma$ and $^2\Pi$. This calculation was made in the minimal basis set of atomic (pseudo-)orbitals. It included $5d_{3/2}, 5d_{5/2}, 6s_{1/2}, 6p_{1/2}$ and $6p_{3/2}$ pseudo-orbitals for Hg or Pb atom and 1s, 2s and 2p orbitals for F atom. All radial functions for fluorine orbitals, for metal pseudo-orbitals and for ARECP were approximated by the sets of Gaussians. After that the MOLCAS package (Roos 1980) was used.

Fourth step: effective spin–orbit potential. In the frame of the RECP method the effective spin–orbit potential can be introduced as follows (Balasubramanian and Pitzer 1987, Ermler

et al 1988):

$$U^{\text{ESOP}}(r) = \sum_{l=0}^{L-1}(U_{l,l-1/2}^{\text{RECP}}(r) + U_{l,l+1/2}^{\text{RECP}^-}(r))\left(\frac{l}{2l+1} \sum_{m=-(l+\frac{1}{2})}^{l+1/2} |l, l + \tfrac{1}{2}, m\rangle\langle l, l + \tfrac{1}{2}, m|\right.$$

$$\left. - \frac{l+1}{2l+1} \sum_{m=-(l-\frac{1}{2})}^{l-1/2} |l, l - \tfrac{1}{2}, m\rangle\langle l, l - \tfrac{1}{2}, m|\right). \tag{6.32}$$

The total molecular Hamiltonian including ARECP and ESOP was diagonalized in the subspace of $^2\Sigma$ and $^2\Pi$ states, thus giving $^2\Sigma_{1/2}$, $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states (in this approximation $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$ states are mixed while the $^2\Pi_{3/2}$ state is a pure state).

Fifth step: restoration of the molecular wavefunction in the core region. The resultant LCAO expansion for the unpaired electron has been used to calculate matrix elements of the PNC interactions. For this purpose the pseudo-orbitals were substituted by the corresponding true orbitals.

This procedure allows us to restore the wavefunction in the core region. An alternative way is to follow the matching procedure of HS. The advantage of the latter method is that one can use a much more flexible basis set of primitive Gaussians. However, the matching radius of HS is smaller than that of the core and thus this matching procedure does not agree with the RECP of the given type. This contradiction can be eliminated with the help of the RECP for the pseudo-orbitals with nodes (Titov *et al* 1991, Mosiagin *et al* 1993, Tupitsin *et al* 1994). In this case the core region is reduced by excluding more than one outer shells from the core. Moreover, as far as RECP includes relativistic effects this matching can be more accurate than for the purely non-relativistic molecular calculations.

Results of the calculations for PbF and HgF. The method described above was used for diatomic radicals PbF and HgF with the ground states $^2\Sigma_{1/2}$ and $^2\Pi_{1/2}$. The accuracy of these calculations was checked by calculating the magnetic hyperfine tensor $\hat{A}$ and the gyromagnetic tensor $\hat{G}$. Several standard spectroscopic characteristics were calculated as

Table 7. Results of the *ab initio* calculations of the constants of the spin–rotational Hamiltonian for the ground states of PbF and HgF molecules.

Constant	PbF	HgF	Units
B^a	6 840	6 540	MHz
$A_\parallel^b$	10 990	24 150	MHz
$A_\perp^b$	−8 990	23 310	MHz
$G_\parallel$	0.040	1.996	—
$G_\perp$	−0.326	1.960	—
D^a	−4.62	−4.15	Debye
W^d	1.4	−4.8	10^{25} Hz e^{-1} cm^{-1}
$W_1^{P,T}$	55	−185	kHz
W_2^P	−720	2 500	Hz
$W^{\mathcal{M}b}$	—	−4.8	10^{33} Hz e^{-1} cm^{-2})

^{a} These parameters are not sensitive to the behaviour of the wavefunction in the core region and were calculated in the basis set of the primitive Gaussians without restoration procedure.
^{b} Magnetic dipole constants A_i are given for spin $\tfrac{1}{2}$ isotopes ^{207}Pb and ^{199}Hg while the magnetic quadrupole constant $W^{\mathcal{M}}$ is given for ^{201}Hg ($I = \tfrac{3}{2}$).

well. In the latter case there was no need to restore the wavefunction in the core region and the basis set of the primitive Gaussians was used.

Results of these calculations for the constants of the spin–rotational Hamiltonian are given in table 7. There is a good agreement with the experiment for the internuclear distance for the PbF molecule. A comparison with the experiment for $G_\perp - G_\parallel$ (HgF) and for $\Delta/2B$ (PbF) shows that there is some overestimation of the spin–orbital mixing. The accuracy of the calculation of the hyperfine constants A and A_d of the HgF molecule is 7% and 14%, respectively. It was shown in the previous section that contribution of the s function is dominant for the constant A while the p function dominates in A_d. So, the accuracy of the results for the PNC terms of the spin–rotational Hamiltonian should be again about 20% or better. Within this accuracy there is agreement between *ab initio* and semi-empirical calculations.

7. Conclusion

The aim of this review is to show that PNC experiments on diatomic molecules can give very important information about fundamental *P*-odd and *P, T*-odd interactions. The main advantage in comparison with atoms is the much larger enhancement factors. Let us compare, for example, the sensitivity to the EDM of the electron in the thallium experiment (Abdullah *et al* 1990) with that in the molecular one. The enhancement factor for Tl is $k \sim 500$. The external electric field is $\mathcal{E}_0 \sim 1 \times 10^5$ V cm^{-1}. So, in the thallium experiment electron is subjected a field of $k\mathcal{E}_0 \sim 5 \times 10^7$ V cm^{-1}. In the molecular experiment it is sufficient to apply the field $\mathcal{E}_0 \sim 2 \times 10^4$ V cm^{-1} to obtain almost complete polarization. Then, the effective electric field on the electron is simply equal to $\frac{1}{2}W_d$ and table 6 gives 3×10^{10} V cm^{-1} for the YbF molecule and 1×10^{11} V cm^{-1} for the HgF molecule.

In table 8 the best experimental upper limits for the constants of the *P, T*-odd interactions as well as the *P, T*-odd moments of the electron and the nuclei are listed together with the equivalent frequency shifts in the molecular experiments. This table shows what are the modern requirements on the accuracy of the molecular experiments. But it should be kept in mind that *P, T*-odd nuclear moments S and $\mathcal{M}$ can differ from one nucleus to another and nuclear calculations are needed for the accurate comparison of the different results.

Another important question is the reliability of the molecular calculations. In the previous section we showed that the accuracy of molecular calculations for the electron-spin-dependent PNC interactions is about 20%. It is sufficient to obtain the upper bounds on the

Table 8. Best experimental upper bounds on the constants of the *P, T*-odd interactions and the equivalent frequency shifts in the molecular experiments.

Constant	Object	Upper bound for the absolute value	Equivalent frequency shift (Hz)		
			TlF	HgF	YbF
S [a]	^{199}Hg	3×10^{-50} e cm^3	5×10^{-5}	—	—
$g_2^{P,T}$ [a]	^{199}Hg	2×10^{-8}	3×10^{-5}	—	—
$g_1^{P,T}$ [a]	^{199}Hg	1×10^{-6}	1×10^{-4}	0.2	0.05
$\mathcal{M}$ [b]	^{133}Cs	1×10^{-34} e cm^2	—	0.5	0.07
d_e [c]	^{203,205}Tl	5×10^{-27} e cm	—	0.3	0.08

[a] Jacobs *et al* (1993).
[b] Peck *et al* (1994).
[c] Commins *et al* (1994).

fundamental constants of the P, T-odd interactions. It is also enough for the measurement of the anapole moment. The situation with the nuclear-spin-dependent P, T-odd interactions is not so favourable. Here reliable calculations are still to be done. But, as we tried to prove, it is possible to do with the help of the existing molecular codes and the new results may appear in the near future.

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