1 SPIN-ORBIT COUPLING AND INTERSYSTEM CROSSING

SPIN-ORBIT INTERACTIONS IN ORGANIC MOLECULES†

H. F. HAMEKA

Forbidden transitions

In spectroscopy the expression 'forbidden transition' is used to describe a transition with a probability that is much smaller than normal. We may indicate how strongly forbidden a transition is by giving the ratio between its probability and the probability of a normal transition; there are cases where this ratio is 10^{-10} or even less. The word 'forbidden' is thus used in a relative sense; in fact, all known forbidden transitions must necessarily have finite transition probabilities.

From a theoretical point of view a transition is forbidden if its probability is zero in zeroth-order approximation and if its magnitude must be evaluated from higher-order approximations. Let us first discuss this zeroth-order approximation. We consider an atom or a molecule containing N electrons; in the case of a molecule we introduce the variable R to denote symbolically the positions of the nuclei. Such a system is described in zeroth-order approximation by the Hamiltonian

$$H_0 = \sum_{j=1}^{N} \frac{p_j^2}{2m} + V(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N; R).\tag{1}$$

We denote the eigenvalues of H_0 by E_n and the corresponding eigenfunctions by Ψ_n. These functions contain the position coordinates $(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$ of the electrons, the electron spin variables $(s_1, s_2, ..., s_N)$ and also the nuclear coordinates R. It follows from the exclusion principle that the functions Ψ_n must be antisymmetric with respect to permutations of the electron coordinates and, consequently, that each

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function Ψ_n must be an eigenfunction of the operators S^2 and S_z. These two operators are defined with the aid of the vector

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \ldots + \mathbf{S}_N, \tag{2}$$

where the operators $\mathbf{S}_j$ define the spins of the individual electrons. Hence

$$S^2 = (\Sigma_j S_{jx})^2 + (\Sigma_j S_{jy})^2 + (\Sigma_j S_{jz})^2,$$

$$S_z = \Sigma_j S_{jz}. \tag{3}$$

In general

$$\left.\begin{aligned} S^2 \Psi_n &= s(s+1)\hbar^2 \Psi_n, \\ S_z \Psi_n &= m_s \hbar \Psi_n, \end{aligned}\right\} \tag{4}$$

where s and m_s are the quantum numbers that label the spin states. Their possible values are

$$\left.\begin{aligned} s &= 0, 1, 2, 3, \ldots, \text{etc.} \quad (N \text{ is even}), \\ s &= \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{5}{2}, \ldots, \text{etc.} \qquad (N \text{ is odd}), \\ m_s &= -s, -s+1, \ldots, s \end{aligned}\right\} \tag{5}$$

It is easily seen that for a given value of s the corresponding spin state is $(2s+1)$-fold degenerate. This number, $2s+1$, is called the multiplicity of the spin state. It is used to identify the eigenvalues of S^2 and is written as a superscript on the left-hand side of the eigenfunction. For example, $^1\Psi_n$ describes a singlet state with $s = 0$, $^2\Psi_{n,j}$ is a doublet state with $s = \tfrac{1}{2}$ and $m_s = j$, $^3\Psi_{n,j}$ is a triplet state with $s = 1$ and $m_s = j$, etc. Different eigenfunctions are orthogonal,

$$\langle {}^k\Psi_{n,i} | {}^l\Psi_{m,j} \rangle = \delta_{n,m} \delta_{k,l} \delta_{i,j}. \tag{6}$$

Also

$$\langle {}^k\Psi_{n,i} | G_{0p}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n, R) | {}^l\Psi_{m,j} \rangle = 0 \tag{7}$$

for different spin states, that is if $k \neq l$ or $i \neq j$, because the spin functions belonging to different spin states are orthogonal.

Let us now consider the calculation of the transition probability between two states (0) and (f). A plane monochromatic light wave may be represented by a vector potential $\mathbf{A}$, which is given as

$$\mathbf{A} = A_0 \, \mathbf{e}\{\gamma \, e^{-2\pi i \nu t} + \gamma^* \, e^{2\pi i \nu t}\} \tag{8}$$

with the abbreviation

$$\gamma = e^{i\boldsymbol{\sigma}\mathbf{r}}. \tag{9}$$

Here $\mathbf{e}$ is a unit vector, which represents the direction of polarisation of the light, $\boldsymbol{\sigma}$ is the wave vector which describes the direction of propagation and also the wavelength,

$$\sigma = 1/\lambda, \tag{10}$$

and ν is the frequency of the light. We have taken the scalar potential of the radiation field equal to zero; this is allowed if we take

$$\operatorname{div} \mathbf{A} = 0, \tag{11}$$

or
$$(\mathbf{e} \cdot \boldsymbol{\sigma}) = 0. \tag{12}$$

The electric and magnetic field strengths of the light wave are given by

$$\mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{H} = \operatorname{curl} \mathbf{A}. \tag{13}$$

Finally, A_0 is a constant, which is a measure of the energy density of the radiation field.

In the presence of an electromagnetic field the Hamiltonian (1) becomes

$$H_1 = \frac{1}{2m}\Sigma_j\left(\mathbf{p}_j + \frac{e}{c}\mathbf{A}_j\right)^2 + V - e\Sigma_j\Phi_j. \tag{14}$$

Here the electromagnetic field is represented by a scalar potential Φ and a vector potential $\mathbf{A}$; Φ_j and $\mathbf{A}_j$ are the potentials experienced by the j-th electron. The perturbation term which is responsible for optical transitions is the term of (14) which is linear in $\mathbf{A}$, that is

$$H_1' = \frac{e}{mc}\Sigma_j\mathbf{A}_j\cdot\mathbf{p}_j. \tag{15}$$

Here and in (14) the charge of the electron is given as $(-e)$.

From (8) and (15) we derive [1] that the time-proportional transition probability between two states (0) and (f) is given by

$$W_{0\rightarrow f} = \frac{e^2}{2\pi m^2 \nu_{0f}^2}H_{f0}H_{f0}^*, \tag{16}$$

with
$$H_{f0} = \langle\Psi_f|\Sigma_j\gamma_j(\mathbf{e}\cdot\nabla_j)|\Psi_0\rangle, \\ h\nu_{0f} = E_f - E_0. \left.\begin{array}{c}\\\\\end{array}\right\} \tag{17}$$

Here E_f and E_0 are the eigenvalues and Ψ_f and Ψ_0 are the eigenfunctions of the states (f) and (0) respectively.

In atoms and molecules the dimensions of the systems are usually much smaller than the wavelength of the light and it is customary to assume that
$$\boldsymbol{\sigma}\cdot\mathbf{r} \ll 1, \quad \gamma_j \approx 1, \tag{18}$$

may be substituted into (17). In that case (17) may be transformed to the customary expression

$$H_{f0} = -(2\pi m\nu_{0f}/e\hbar)(\mathbf{e}\cdot\mathbf{P}_{f0}), \\ \mathbf{P}_{f0} = \langle\Psi_f|e\Sigma_j\mathbf{r}_j|\Psi_0\rangle, \left.\begin{array}{c}\\\\\end{array}\right\} \tag{19}$$

where $\mathbf{P}_{f0}$ is called the transition moment between the states (0) and (f).

We call a transition forbidden if the transition moment (19) is equal to $\mathbf{0}$. It is possible that $\mathbf{P}_{f0}$ is $\mathbf{0}$ by coincidence, but this is very unlikely and we do not consider this. Otherwise there are two possible reasons that can cause the transition moment to be zero. The first one is a difference in spin quantum numbers between the states (0) and (f); we speak then of spin-forbidden transitions. The second reason is that the integration over the electron position coordinates in (19) gives zero because of the symmetries of the states (0) and (f); in that case the transition is called symmetry-forbidden.

The above discussion is based on the zero-order approximation, and we mentioned already that the finite probabilities of forbidden transitions can be explained only by considering higher-order approximations. In the case of spin-forbidden transitions we ought to consider more accurate Hamiltonians than H_0 of (1) and H_1 of (14) in order to derive a satisfactory theory. In the case of symmetry-forbidden transitions we can arrive at finite transition probabilities by using (17), and there is no need to consider higher-order terms of the Hamiltonian. Here there are two mechanisms that make the transition possible. The first mechanism is derived by observing that the approximation (18) is inadequate and that instead we ought to substitute

$$\gamma_j \approx 1 + i(\boldsymbol{\sigma} . \mathbf{r}_j) \tag{20}$$

into (17). We obtain then

$$H_{f0} = \langle \Psi_f | i\Sigma_j (\boldsymbol{\sigma} . \mathbf{r}_j) (\mathbf{e} . \boldsymbol{\nabla}_j) | \Psi_0 \rangle \tag{21}$$

since the first term on the right-hand side of (20) gives zero if the transition is forbidden. Transitions that are described by (21) are called magnetic dipole or electric quadrupole transitions, as opposed to electric dipole transitions, which are described by equations (19).

In molecules there exists a second mechanism that can make a symmetry-forbidden transition possible, namely, the molecular vibrations. The symmetry rules for the electronic wavefunctions are derived on the assumption that the nuclei are fixed at their equilibrium positions and the small, but finite, motion of the nuclei has the effect of distorting the symmetry of the electronic wavefunctions and to make the transition possible. We speak here of a vibrationally-allowed forbidden transition.

In the following section we will discuss the theory of spin-forbidden

transitions, and we will see that the general theory of forbidden transitions is exactly the same for atoms and for molecules. In practice, on the other hand, there are important differences between atoms and molecules because the orders of magnitude of the various effects that make forbidden transitions observable are quite different in the two cases. In an atom a symmetry-forbidden transition can occur only as an electric quadrupole or a magnetic dipole transition, and this means that the transition probability is at most 10^{-6} times the probability of an allowed transition. In a molecule a symmetry-forbidden transition can be made possible by vibrations or a number of other effects and the probability varies between 10^{-4} and 10^{-1} times a normal transition probability. Consequently the symmetry restrictions are much more rigid for atoms than for molecules.
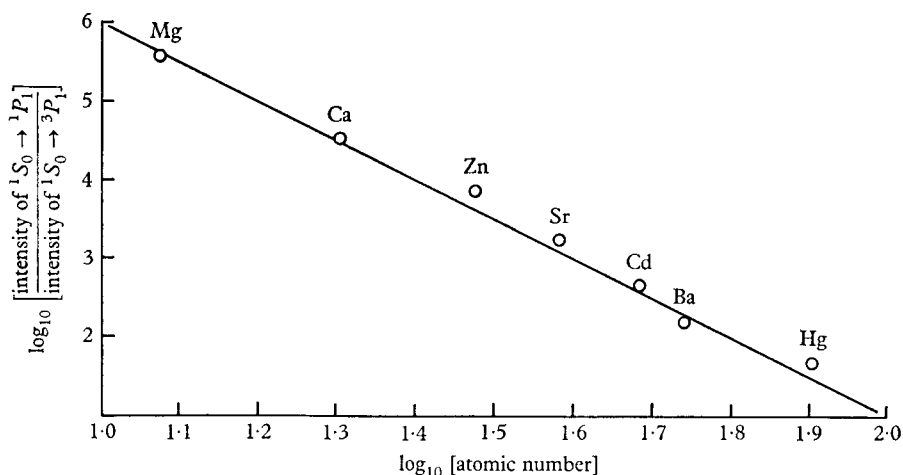

Fig. 1. A log-log plot illustrating the effect of atomic number on the intensity of a spin-forbidden transition.[2]

The general theory of spin-forbidden transitions is the same for atoms and molecules, but a very important difference between an atom and a molecule is due to the central symmetry of an atom as opposed to a molecule. As a consequence we are able to transform the theory of spin-forbidden transitions in atoms to a much simpler form than we can do for molecules. It is important to recognise that the detailed theoretical expressions for atoms cannot be applied to molecules since they were derived on the assumption that the system under consideration possesses central symmetry. A misappreciation of this point has led to some confusion in the literature. The prob-

ability, or intensity, of a spin-forbidden transition varies widely between different atoms. For example, in fig. 1 we have plotted[2] the intensity ratio between the $^1S_0 \to {}^3P_1$ and the $^1S_0 \to {}^1P_1$ transitions in a number of atoms; it is shown that this ratio varies between 10^{-6} and 10^{-1} and that it is inversely proportional to the fifth power of the atomic number Z. We usually consider spin-forbidden transitions in organic molecules only where the atoms are fairly light ($Z < 10$). Here the probabilities of spin-forbidden transitions vary between 10^{-5} and 10^{-10} times the probabilities of allowed transitions.

It follows from the above orders of magnitude that any molecular transition with a probability that is less than 10^{-5} times a normal transition is very likely spin-forbidden. In heavy atoms spin-forbidden transitions are almost as intense as normal transitions, and much more intense than symmetry-forbidden transitions. In light and inter-mediate atoms spin-forbidden and symmetry-forbidden transitions have comparable probabilities.

Spin interactions in the Hamiltonian

The finite probabilities of spin-forbidden transitions can be under-stood only if we base our considerations on Hamiltonians that are more accurate than the ones reported in equations (1) and (14). More specifically, we must derive the parts of the Hamiltonian that depend on the electron spin. The derivation of these spin-interaction terms is a straightforward problem, which has been solved satisfactorily in a number of different ways. However, there seems to be some confusion in the literature as to the correct form of the spin Hamiltonian for molecules. This confusion stems from the fact that in an atom the spin Hamiltonian can be transformed further because of the central sym-metry and that attempts to use these atomic spin Hamiltonians for molecules led to inconsistent results. We have even encountered statements in the literature[3] which claim that the spin Hamiltonian for a molecule is not known. These statements are obviously incorrect since the general form of the spin Hamiltonian, valid for both atoms and molecules, has been known since the late twenties.

We mentioned already in the previous section that the angular momentum of a spinning electron is represented by an operator $\mathbf{S}$. For a single electron the quantum number s, defined by equation (4), is $\frac{1}{2}$ and the possible values of the other quantum number m_s are $m_s = \pm \frac{1}{2}$. We denote the two eigenfunctions of S_z by α and β. By drawing an

analogy with the properties of the orbital angular momentum operator it may then be derived that

$$S_x\alpha = \tfrac{1}{2}\hbar\beta, \quad S_y\alpha = \tfrac{1}{2}i\hbar\beta, \quad S_z\alpha = \tfrac{1}{2}\hbar\alpha, \atop S_x\beta = \tfrac{1}{2}\hbar\alpha, \quad S_y\beta = -\tfrac{1}{2}i\hbar\alpha, \quad S_z\beta = -\tfrac{1}{2}\hbar\beta.} \tag{22}$$

A spinning electron possesses also a magnetic moment $\boldsymbol{\mu}$, which is related to $\mathbf{S}$ by means of

$$\boldsymbol{\mu} = (-e/mc)\,\mathbf{S}. \tag{23}$$

This expression was first proposed by Goudsmit & Uhlenbeck[4] because it leads to a satisfactory explanation of the experimental data; it can be derived from the Dirac equation and it was also obtained by Kramers[5] from a non-quantum mechanical, relativistic, argument.

Let us first derive the spin Hamiltonian of an electron with a charge $(-e)$ that moves with a velocity $\mathbf{v}$ in a circular orbit around a nucleus with a charge Ze. We first observe that a magnetic moment $\boldsymbol{\mu}$ at rest in a magnetic field $\mathbf{H}$ has the energy

$$E_\mu = -\boldsymbol{\mu}.\mathbf{H}. \tag{24}$$

It follows from equations (23) and (24) that the spin energy of an electron at rest, in the presence of an electromagnetic field $(\mathbf{E}, \mathbf{H})$, is given by

$$E_s = (e/mc)\,(\mathbf{S}.\mathbf{H}). \tag{25}$$

If the electron moves with a velocity $\mathbf{v}$ with respect to the nucleus then it seems to an observer who is stationed on the electron that the nucleus moves with a velocity $-\mathbf{v}$. This motion gives rise to a magnetic field

$$\mathbf{H} = -\frac{Ze}{c}\frac{\mathbf{v}\times\mathbf{r}}{r^3}, \tag{26}$$

where $\mathbf{r}$ is the distance from the nucleus to the electron. According to this argument the spin energy of the electron becomes

$$E_s = \frac{-Ze^2}{mc^2}\frac{(\mathbf{v}\times\mathbf{r}).\mathbf{S}}{r^3}. \tag{27}$$

However, this result is incorrect. Equation (27) was derived from the point of view of an observer stationed on the electron, and the correct result should have been derived from the point of view of an observer stationed on the nucleus. This makes a difference because to an observer on the nucleus it appears that the coordinate system where the electron is at rest rotates with a frequency[6]

$$\boldsymbol{\omega}_T = (1/2c^2)\,(\mathbf{v}\times\mathbf{a}). \tag{28}$$

This is called the Thomas frequency. The acceleration **a** of the electron may be replaced by

$$\mathbf{a} = Ze^2\mathbf{r}/r^3m, \tag{29}$$

so that

$$\boldsymbol{\omega}_T = \frac{Ze^2}{2mc^2}\frac{\mathbf{v}\times\mathbf{r}}{r^3}. \tag{30}$$

This means that the electron experiences in addition to the magnetic field **H** of equation (26) a field

$$\mathbf{H}_T = \frac{Ze}{2c}\frac{\mathbf{v}\times\mathbf{r}}{r^3}. \tag{31}$$

Consequently it experiences a total magnetic field

$$\mathbf{H}' = \mathbf{H} + \mathbf{H}_T = -\frac{Ze}{2c}\frac{\mathbf{v}\times\mathbf{r}}{r^3} \tag{32}$$

and its energy is

$$E'_s = -\frac{Ze^2}{2mc^2}\frac{(\mathbf{v}\times\mathbf{r}).\mathbf{S}}{r^3}. \tag{33}$$

Equation (33) differs from equation (27) by a factor of one half, which is known as the Thomas factor. Finally we introduce the angular momentum

$$\mathbf{L} = m(\mathbf{r}\times\mathbf{v}) \tag{34}$$

of the electron and we write (33) as

$$E'_s = \frac{Ze^2}{2m^2c^2r^3}(\mathbf{L}.\mathbf{S}) = \xi(r)\,\mathbf{L}.\mathbf{S}. \tag{35}$$

This is the well-known expression for the spin-orbit coupling of an electron in a central force field. It is important to realise that equation (35) is neither valid for non-central force fields nor for many-electron systems.

It was shown by Thomas[6] and, subsequently, by Kramers[5] that the general expression for the spin energy of an electron in an electro-magnetic field (**E**, **H**) is given by

$$E'_s = \frac{e}{mc}\mathbf{S}.\left\{\mathbf{H} + \frac{1}{2c}(\mathbf{E}\times\mathbf{v})\right\}. \tag{36}$$

This result is again consistent with the Dirac equation. We may combine this with equation (14) in order to obtain the total Hamiltonian H of an electron in an electromagnetic field. The field is given by the field strengths **E** and **H** or by the scalar potential Φ and the vector potential **A**. The Hamiltonian is

$$H = \frac{1}{2m}\left(\mathbf{p}+\frac{e}{c}\mathbf{A}\right)^2 - e\Phi + \frac{e}{mc}\mathbf{S}.\left\{\mathbf{H}+\frac{1}{2mc}(\mathbf{E}\times\mathbf{p})\right\}. \tag{37}$$

For example, this is the proper Hamiltonian for the hydrogen molecular ion if we take the electromagnetic field as the sum of the fields of the two nuclei and the exterior field.

Let us now generalise the Hamiltonian (37) to a molecule with N electrons, represented by the coordinates $\mathbf{r}_j$ and the momenta $\mathbf{p}_j$ and with N' nuclei, represented by the coordinates $\mathbf{R}_n$. We assume that the nuclei are at rest so that they give rise to an electric field $\mathbf{F}$ only. In addition, there is an exterior field, which is derived from the potentials Φ and $\mathbf{A}$ and which has an electric field strength $\mathbf{E}$ and a magnetic field strength $\mathbf{H}$. The total Hamiltonian for the molecule is then represented as

$$H = H_0 + H_{\text{int.}} + H_{\text{s.o.}} + H_{\text{s.s.}}. \tag{38}$$

Here H_0 is the zero-order Hamiltonian

$$H_0 = \frac{1}{2m}\sum_{i=1}^{N} p_i^2 + e^2\left[-\sum_{i=1}^{N}\sum_{n=1}^{N'}\frac{Z_n}{r_{n,i}} + \sum_{i>j}\frac{1}{r_{i,j}} + \sum_{n>k}\frac{Z_n Z_k}{R_{n,k}} \right]. \tag{39}$$

Here we have introduced

$$\mathbf{r}_{i,j} = \mathbf{r}_j - \mathbf{r}_i, \quad \mathbf{r}_{n,i} = \mathbf{r}_i - \mathbf{R}_n, \quad \mathbf{R}_{n,k} = \mathbf{R}_k - \mathbf{R}_n. \tag{40}$$

The electric charge on nucleus n is eZ_n.

The interaction between the orbital motion of the electrons and the exterior electromagnetic field is represented by

$$H_{\text{int.}} = \sum_j\left[\frac{e}{mc}\mathbf{A}_j\,\mathbf{p}_j + \frac{e^2}{2mc^2}A_j^2 - e\Phi_j \right]. \tag{41}$$

The spin-dependent parts of the Hamiltonian are $H_{\text{s.o.}}$, which is linear in the spin operators and which is called the spin-orbit inter-action, and $H_{\text{s.s.}}$, which is quadratic in the spin operators and which is called the spin-spin interaction. We write the spin-orbit interaction as

$$H_{\text{s.o.}} = \frac{e}{mc}\sum_j \mathbf{S}_j \cdot \mathbf{B}_j \tag{42}$$

with

$$\mathbf{B}_j = \mathbf{H}_j + \frac{1}{2mc}[\mathbf{E}_j \times \mathbf{p}_j] + \frac{1}{2mc}[\mathbf{F}_j \times \mathbf{p}_j]$$
$$+ \frac{e}{mc}\sum_{k\neq j} r_{j,k}^{-3}[(\mathbf{p}_k - \tfrac{1}{2}\mathbf{p}_j) \times \mathbf{r}_{j,k}]. \tag{43}$$

The term $H_{\text{s.s.}}$ is quadratic in the spin operators; it is called the spin-spin interaction since it represents the interactions between different electron spins. Its form is

$$H_{\text{s.s.}} = (e^2/m^2c^2)\sum_i\sum_{j>i} r_{i,j}^{-5}\{r_{i,j}^2(\mathbf{S}_i \cdot \mathbf{S}_j) - 3(\mathbf{r}_{i,j} \cdot \mathbf{S}_i)(\mathbf{r}_{i,j} \cdot \mathbf{S}_j)\}$$
$$- (8\pi e/3mc)\sum_i\sum_{j>i}(\mathbf{S}_i \cdot \mathbf{S}_j)\,\delta(\mathbf{r}_{i,j}). \tag{44}$$

The second sum of equation (44) is called the Fermi contact potential; it can be derived from classical electromagnetic theory if the finite dimensions of the electrons are taken into consideration.

The Hamiltonian defined by (38) and subsequent equations has been derived also from quantum electrodynamics [7] by means of a relativistic expansion. Here it is assumed that the electron velocities v are small compared with the light velocity c so that it is possible to expand the Hamiltonian as a power series in (v/c). The first terms of this power series expansion constitute the Hamiltonian H of equation (38). Even though the Hamiltonian H is not complete, since there are always terms of higher order that should be added to it, there is no doubt that it is correct as long as $v \ll c$.

Most of the confusion in the literature with regard to the spin-orbit interaction stems from attempts to approximate (42) and (43) for atoms. We have seen in equation (35) that for the hydrogen atom the spin-orbit coupling can be expressed as the scalar product of $\mathbf{L}$ and $\mathbf{S}$. This has led to the approximation

$$H_{\text{s.o.}} \approx \sum_{j=l}^{N} \xi(r_j)\, \mathbf{L}_j . \mathbf{S}_j \tag{45}$$

for an arbitrary atom. However, if we rewrite equation (43) for an atom, taking $\mathbf{E}$ and $\mathbf{H}$ equal to zero,

$$\mathbf{B}_j = (e/2mc)\Bigg[\Big(Zr_j^{-3} - \sum_{k\neq j} r_{j,k}^{-3} \Big)\mathbf{L}_j - 2\sum_{k\neq j} r_{j,k}^{-3}\mathbf{L}_k \\ + \sum_{k\neq j} r_{j,k}^{-3}\{2(\mathbf{r}_j \times \mathbf{p}_k) - (\mathbf{r}_k \times \mathbf{p}_j)\} \Bigg] \tag{46}$$

we see what the shortcomings of this approximation are. Only the first term of (46) leads to an expression of the form (45), namely

$$H_{\text{s.o.}}^0 = (e^2/2m^2c^2) \sum_{j} (Zr_j^{-3} - \sum_{k\neq j} r_{j,k}^{-3})\, (\mathbf{L}_j . \mathbf{S}_j), \tag{47}$$

but it is not obvious why the other terms may be neglected. The second term of (46) gives a contribution

$$H_{\text{s.o.}} = (-e^2/m^2c^2) \sum_{j} \sum_{k\neq j} r_{j,k}^{-3}(\mathbf{L}_k . \mathbf{S}_j) \tag{48}$$

to the spin-orbit coupling. This is called the spin-other orbit coupling and it is sometimes taken into account in atomic theory. However $H_{\text{s.o.}}$ contains still an additional term

$$H_{\text{s.o.}}^2 = (e^2/2m^2c^2) \sum_{j} \sum_{k\neq j} r_{j,k}^{-3}\{2(\mathbf{r}_j \times \mathbf{p}_k) - (\mathbf{r}_k \times \mathbf{p}_j)\} . \mathbf{S}_j, \tag{49}$$

which fits neither into (47) nor into (48).