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Contribution of the individual discrete levels to the Lamb shift in hydrogen atoms

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Abstract. We have evaluated explicitly the transition form factors $T^{\mu}_{mn}(\boldsymbol{k})$, or the Fourier components of the transition currents, between states m and n, and with them, the contribution of an individual level m to the Lamb shift of level n, including the retardation exponentials.

1. Introduction

The purpose of this work is to evaluate explicitly the contribution of individual discrete states to the Lamb shift of a given state in hydrogen-like atoms. The Lamb shift is usually calculated, using sum rules or Green function method, as an infinite sum over discrete and continuous spectrum, which gives us no intuitive feeling for the nature and magnitude of each contribution. To our knowledge, these terms of the Lamb shift have not been studied in detail. The individual contributions cannot be calculated in Bethe's original form because the integrals diverge. Moreover, it may also be possible in the near future to measure the individual contributions to the Lamb shift [1] experimentally. As a byproduct our calculations also give the transition form factors $T^{\mu}_{mn}(\boldsymbol{k})$ or Fourier transform of the transition currents between two states m and n without the dipole approximation which are useful in many other applications. These results also implicitly contain the electromagnetic field produced by the atom in a transition process, which will be studied further in a sequel to this work.

We shall use the self-field approach to quantum electrodynamics (QED). The underlying physical picture is that one adds the field produced by the current $j_\mu = e\bar{\psi}\gamma_\mu\psi$ of the bound electron to the external field. However, the formulae for the Lamb shift in the lowest order α in coupling (but to all orders of $Z\alpha$ in wavefunction) are the same as in standard perturbative QED [2–5]. There are some conceptual simplifications and the integrals are regularized in a simpler way. The retardation is kept so that the theory is finite.

It is not our purpose here to present a precise value for the total Lamb shift and compare it with experiment. For this we refer to recent excellent numerical calculations [6, 7]. Rather we wish to improve our conceptual and quantitative understanding of the various contributions (discrete–continuous, electric–magnetic, low energy, high energy) that make up the total Lamb shift, and the various approaches to the problem.

We therefore give in this introduction a brief overview of the situation. The Lamb shift δE_n of a quantum level n is usually computed from the following parts [2, 3].

(a) The electric low-frequency component (Bethe–Salpeter [4], equation (19.7)). For an s-state $n(l-0)$:

$$W_1 + W_2 \equiv -D\left[\int_0^\lambda dk\,\langle p^2\rangle_{nn} - \sum_\nu P_{n\nu}\int_0^\lambda \frac{dk}{E_\nu - E_n + kc}\right] \tag{1}$$

where D is the constant $2\alpha Z^4/(3\pi m^2 c)$ and $P_{n\nu}$ is defined as

$$P_{n\nu} \equiv \boldsymbol{p}_{n\nu}\cdot\boldsymbol{p}_{\nu n}(E_\nu - E_n) \tag{2}$$

$\boldsymbol{p}_{n\nu}$ is the matrix element $\langle n|\boldsymbol{p}|\nu\rangle$ and $\lambda \ll mc$ is a cut-off momentum. The summation over states must be performed over the discrete levels ν and the continuum spectrum, so that the second term W_2 in (1) is

$$W_2 = \sum_\nu \delta E_{n\nu} + \delta E_n^{\text{continuum}} \tag{3}$$

$$\delta E_{n\nu} = D(E_\nu - E_n)\int_0^\lambda dk\,\frac{\bar{p}_{n\nu}\cdot\bar{p}_{\nu n}}{kc + E_\nu - E_n}. \tag{4}$$

Performing the integration over k in (1), and neglecting $E_\nu - E_n$ with respect to λc in $\ln(\lambda c + E_\nu - E_n)$ leads to

$$W_2 = D\sum_\nu P_{n\nu}\left[\ln\frac{\lambda c}{mc^2} - \ln\frac{E_\nu - E_n}{Z^2 Ry} - \ln\frac{\alpha^2 Z^2}{2}\right]. \tag{5}$$

The Bethe logarithm $\ln(k_0/Z^2 Ry)$ is then defined in such a way that (5) is exactly equal to

$$W_2 = D\left(\sum_\nu P_{n\nu}\right)\left[\ln\frac{\lambda c}{mc^2} - \ln\frac{k_0}{Z^2 Ry} - \ln\frac{\alpha^2 Z^2}{2}\right]. \tag{6}$$

(b) A mass renormalization term W_3 ([4], equation (19.8 bis)), which exactly cancels the first term W_1 in (1).

(c) High energy and higher order terms. Relativistic terms and vacuum polarization ([4], equations (18.2) and (19.3)):

$$W_4 \equiv -\left(\frac{\hbar}{mc}\right)^2\frac{\alpha}{3\pi}\left[\ln\frac{mc^2}{\lambda c} - \ln 2 - \frac{3}{8} + \frac{5}{6} - \frac{1}{5}\right]e\langle\Delta\varphi\rangle_{nn} \tag{7}$$

λ is the same cut-off momentum matched to the cut-off in (1). The vacuum polarization term $-\frac{1}{5}$ is discussed in the self-energy formalism in [8].

(d) A magnetic term due to the anomalous moment of the electron: ([4], equation (21.3); [9])

$$W_5 \equiv \frac{\alpha^5 mc^2}{2\pi n^3}Z^4\frac{c_{lj}}{2l+1} \tag{8}$$

with $c_{lj} = -1/l$ for $j = l - \frac{1}{2}$ and $c_{lj} = 1/(l+1)$ for $j = l + \frac{1}{2}$.

The same formulae (6), (7) and (8) apply to a p-state ($n, l = 1$), but the terms $-\ln(\alpha^2 Z^2)$ and $(\frac{11}{24} - \frac{1}{5})$ must then be suppressed in (6) and (7).

In the self-field formulation, when the potential A_μ is eliminated between the coupled Maxwell and Dirac (or Schrödinger) equations, one obtains a non-linear equation

$$(\gamma^\mu(\mathrm{i}\partial_\mu - eA_\mu^{\mathrm{ext}}) - m)\psi = e\gamma^\mu\psi \int \mathrm{d}y\, D(x-y)\bar{\psi}(y)\gamma_\mu\psi(y)$$

where A_μ^{ext} is a fixed external field and $D(x-y)$ is the Green function of the d'Alembertian. The treatment of all QED effects (Lamb shift, spontaneous emission, $g-2$, vacuum polarization, etc) are based on an analysis of the single non-linear term in the right-hand side of this equation (for a recent review see [10]). The non-relativistic form of this non-linear equation was studied in detail in [11], and we base our calculations on these results.

2. Method of calculation of the discrete contributions

The non-relativistic Barut and Van Huele formula [11]

$$\delta E_{n\nu} = \frac{-e^2}{4\pi\varepsilon_0} \frac{\hbar h^3 \omega_{n\nu}}{4\pi^2 m^2 c} \int \frac{\mathrm{d}^3 \boldsymbol{k}}{k^2} \frac{\boldsymbol{T}_{\nu n}^{\perp}(-\boldsymbol{k}) \cdot \boldsymbol{T}_{n\nu}^{\perp}(\boldsymbol{k})}{\omega_{n\nu} - k} \tag{9}$$

gives the contribution of each discrete level ν to the shift, so that the total Lamb shift of a quantum level n is

$$\delta E_n = \sum_\nu \delta E_{n\nu} + \delta E_n^{\mathrm{continuum}}. \tag{10}$$

In (10), m is the electron mass, $\omega_{n\nu} \equiv (E_n - E_\nu)/\hbar_C$ is the transition frequency, and $k \equiv |\boldsymbol{k}|$; $\boldsymbol{T}_{\nu n}^{\perp}$ represents the component perpendicular to $\boldsymbol{k}$ of the form factor

$$\boldsymbol{T}_{\nu n}(\boldsymbol{k}) \equiv \int \mathrm{d}^3\boldsymbol{x}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \psi_\nu^*(\boldsymbol{x}) \nabla \psi_n(\boldsymbol{x}). \tag{11}$$

By convention, $1/(\omega_{n\nu} - k)$ must be taken as the principal value of (1) when $E_n > E_\nu$ (i.e. $\omega_{n\nu} > 0$).

When the retardation exponentials $\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{n}}$ are replaced by unity in (11), expression (4) is obtained, in which a cut-off was necessary. That is now eliminated.

The single contribution $\delta E_{1\mathrm{s}\,2\mathrm{p}}$ of level $\nu \equiv (2\mathrm{p})$ to the energy shift of level $n \equiv (1\mathrm{s})$ has been calculated previously [12] (in this reference, expression (20) for $\delta E_{1\mathrm{s}3\mathrm{p}}$ is incorrectly multiplied by a factor 2, because of incorrectly normalized hydrogen orbitals taken from [13]) using (9). Here we will generalize this calculation to any orbitals n and ν and study the nature of various contributions and their properties. The following two different situations occur.

(i) First case. The two orbitals ψ_n and ψ_ν have a common axis of cylindrical symmetry (examples: $|n\rangle = \mathrm{s}$ and $|\nu\rangle = \mathrm{p}, \mathrm{d}$ or f; $n = \mathrm{p}$ and $\nu = \mathrm{p}$ with the same axis; etc).

Let $\boldsymbol{e}_3$ be the unit vector on this axis of symmetry, and β ($0 \leqslant \beta \leqslant \pi$) the angle between $\boldsymbol{k}$ and $\boldsymbol{e}_3$; and let $\boldsymbol{j}$ be the unit vector orthogonal to $\boldsymbol{k}$ and contained in the half-plane of edge $\boldsymbol{k}$ and containing $\boldsymbol{e}_3$. By symmetry $\boldsymbol{T}^{\perp}_{n\nu}$ is parallel to $\boldsymbol{j}$, and is more precisely in the form

$$\boldsymbol{T}^{\perp}_{n\nu}(\boldsymbol{k}) = \boldsymbol{j}\sum_i f_{n\nu,i}\ (\beta) t_{n\nu,i}(k) \tag{12}$$

with finite summation $\sum_i$. Here the functions f and t are given in appendix B.

For example, for orbitals of types s and p we have ($n \equiv n$s and $\nu \equiv \nu$p)

$$\boldsymbol{T}^{\perp}_{n\nu}(\boldsymbol{k}) = \boldsymbol{j}\sin\beta t_{n\nu}(\boldsymbol{k}) \qquad \text{(real vector).} \tag{13}$$

For orbitals of type p with the same axis ($n \equiv n\mathrm{p}_z$ and $\nu \equiv \nu\mathrm{p}_z$), we have

$$\boldsymbol{T}^{\perp}_{n\nu}(\boldsymbol{k}) = \mathrm{i}\,\boldsymbol{j}\sin\beta\cos\beta\ t_{n\nu}(\boldsymbol{k}) \qquad \text{(imaginary vector).} \tag{14}$$

When (4) is inserted into (1), the integral over $\boldsymbol{k}$ becomes

$$\int_{\boldsymbol{k}} = 2\pi\sum_i\sum_j\left[\int_0^{\pi}\mathrm{d}\beta\sin\beta f_{\nu n,i}(\pi-\beta)f_{\nu n,j}(\beta)\right]\int_0^{\infty}\frac{\mathrm{d}k}{\omega_{n\nu}-k}t_{\nu n,i}(k)t_{n\nu,j}(k). \tag{14a}$$

(ii) Second case. The orbitals n and ν have cylindrical symmetry axes $\boldsymbol{e}_0$ and $\boldsymbol{e}_3$ ($|\boldsymbol{e}_0| = 1 = |\boldsymbol{e}_3|$ is assumed) which are perpendicular to each other. In integral (9), the vector $\boldsymbol{k}$ takes all orientations in a frame bound to the axes $\boldsymbol{e}_0$ and $\boldsymbol{e}_3$ of the orbitals. The integration of (11) at first seems to be complicated in the general case where $\boldsymbol{k}$ has any orientation with respect to the fixed axes $\boldsymbol{e}_0$ and $\boldsymbol{e}_3$. However, a suitable transformation allows us to restrict the calculation of $\boldsymbol{T}^{\perp}(\boldsymbol{k})$ either to the case of $\boldsymbol{k}$ orthogonal to one of the two axes, or to the case where $\boldsymbol{k}, \boldsymbol{e}_0$ and $\boldsymbol{e}_3$ are coplanar.

For any orientation of $\boldsymbol{k}$ let us define the vector $\boldsymbol{j}$ as indicated previously, and the unit vectors $\boldsymbol{i}$ and $\boldsymbol{j}'$ as

$$\boldsymbol{i} \equiv \boldsymbol{j}\times\frac{\boldsymbol{k}}{k} \qquad \text{and} \qquad \boldsymbol{j}' \equiv \boldsymbol{e}_3\times\boldsymbol{i}. \tag{15}$$

The orientation of $\boldsymbol{k}$ with respect to the $\boldsymbol{e}_3$ and $\boldsymbol{e}_0$ axes of the orbitals is measured in spherical coordinates $(k, \beta, \frac{3}{2}\pi - \varphi_0')$ by the angle β between $\boldsymbol{e}_3$ and $\boldsymbol{k}$, and by the angle $\frac{3}{2}\pi - \varphi_0'$ $(0 \leqslant \varphi_0' \leqslant 2\pi)$ of rotation around $\boldsymbol{e}_3$ which moves $\boldsymbol{e}_0$ to $-\boldsymbol{j}'$.

In the plane orthogonal to $\boldsymbol{e}_3$ we therefore have

$$\varphi_0' \equiv \text{angle }(\boldsymbol{i}, \boldsymbol{e}_0)$$

$$\frac{\pi}{2} - \varphi_0' \equiv \text{angle }(\boldsymbol{e}_0, \boldsymbol{j}')$$

$$\frac{3\pi}{2} - \varphi_0' \equiv \text{angle }(\boldsymbol{e}_0 - \boldsymbol{j}')$$

where $-\boldsymbol{j}'$ is the normalized projection of $\boldsymbol{k}$. To simplify the notations we shall write

$$\boldsymbol{k} \equiv (k, \beta, \varphi_0') \qquad \text{instead of} \qquad \boldsymbol{k} \equiv \left((k, \beta, \tfrac{3}{2}\pi - \varphi_0'\right).$$

In (9) we have

$$\int_{\boldsymbol{k}} = \int_0^{2\pi} (-\mathrm{d}\varphi_0') \int_0^{\pi} \mathrm{d}\beta \, \sin\beta \int_0^{\infty} \mathrm{d}k \, \frac{k^2}{k^2(\omega_{n\nu} - k)} \boldsymbol{T}^{\perp}_{\nu n}(k, \pi-\beta, \varphi_0'+\pi) \cdot \boldsymbol{T}^{\perp}_{n\nu}(k, \beta, \varphi_0'). \tag{16}$$

In the frame $(\boldsymbol{i}, \boldsymbol{j}', \boldsymbol{e}_3)$ fixed to $\boldsymbol{e}_3$ and $\boldsymbol{k}$, the orbital $n \equiv (nlm)$ can be written as

$$\begin{aligned} n(r, \theta', \varphi') = a(r, \theta') \cos(m(\varphi' - \varphi_0')) \\ = a(r, \theta')[\cos(m\varphi')\cos(m\varphi_0') + \sin(m\varphi')\sin(m\varphi_0')] \\ = \cos(m\varphi_0') n_x + \sin(m\varphi_0') n_y \end{aligned} \tag{17}$$

where n_x and n_y are the orbitals $n \equiv (nlm)$ having axes $\boldsymbol{i}$ and $\boldsymbol{j}'$, respectively. Consequently

$$\begin{aligned} \boldsymbol{T}^{\perp}_{n\nu}(k, \beta, \varphi_0') = \cos(m\varphi_0')\boldsymbol{T}^{\perp}_{n\nu}(k, \beta, 0) + \sin(m\varphi_0')\boldsymbol{T}^{\perp}_{n\nu}\left(k, \beta, \tfrac{1}{2}\pi\right) \\ \equiv \cos(m\varphi_0')\boldsymbol{T}^{\perp}_{n_x\nu}(k, \beta) + \sin(m\varphi_0')\boldsymbol{T}^{\perp}_{n_y\nu}(k, \beta) \end{aligned} \tag{18}$$

$$\boldsymbol{T}^{\perp}_{\nu n}(k, \pi - \beta, \varphi_0' + \pi) = (-1)^m[\cos(m\varphi_0')\boldsymbol{T}^{\perp}_{\nu n_x}(k, \pi - \beta) + \sin(m\varphi_0')\boldsymbol{T}^{\perp}_{\nu n_y}(k, \pi - \beta)]. \tag{19}$$

Let us now substitute (18) and (19) into (16). The cross terms are zero, since

$$\int_0^{2\pi} \mathrm{d}\varphi_0' \cos(m\varphi_0') \sin(m\varphi_0') = 0.$$

The remaining terms are

$$\begin{aligned} \int_{\boldsymbol{k}} = (-1)^m \pi \int_0^{\infty} \frac{\mathrm{d}k}{\omega_{n\nu} - k} \int_0^{\pi} \mathrm{d}\beta \, \sin\beta \Big[\boldsymbol{T}^{\perp}_{n\nu}(k, \pi - \beta, 0) \cdot \boldsymbol{T}^{\perp}_{n\nu}(k, \beta, 0) \\ + \boldsymbol{T}^{\perp}_{n\nu}\left(k, \pi - \beta, \frac{\pi}{2}\right) \cdot \boldsymbol{T}^{\perp}_{n\nu}\left(k, \beta, \frac{\pi}{2}\right) \Big]. \end{aligned} \tag{20}$$

Equation (20), unlike (9), no longer necessitates the calculation of $\boldsymbol{T}^{\perp}(\boldsymbol{k})$ for any $\boldsymbol{k}$, but only for the special orientations of $\boldsymbol{k}$ (with respect to $\boldsymbol{e}_3$ and $\boldsymbol{e}_0$) described earlier.

By symmetry, the $\boldsymbol{T}^{\perp}$ in (20) are parallel to $\boldsymbol{j}$. They can still be put in the form (12) (appendix B). Substitution of (12) into (20) gives a sum of double integrals $\int_k \int_\beta$ which can be factorized, as in (14a).

3. Values of the $\delta E_{n\nu}$: discussion

The form factors $\boldsymbol{T}^{\perp}_{n\nu}$ are calculated (appendix B) for the low levels of the atom, $n, \nu =$ 1s, 2s, 2p, 3s, 3p. For $n =$ 2p and $\nu =$ 3p the calculation is made in both cases where orbitals n and ν have parallel and perpendicular symmetry axes.

The shifts $\delta E_{n\nu}$ corresponding to these values of n and ν are then calculated in appendix E. Several general properties must be noticed.

(i) For two s orbitals, $\delta E_{ns\ \nu s}$ is zero, because $\boldsymbol{T}^{\perp}$ is zero (see (B1)).

(ii) Any two levels n, ν have mutual energy shifts that are nearly opposite:

$$\delta E_{n\nu} \simeq -\delta E_{\nu n}. \tag{21}$$

As an example, let us establish this property for orbitals of types s and p, for which $\boldsymbol{T}^{\perp}$ is in the form (13). Let n be the lower level ($E_n < E_\nu$). Substitution of (13) into (9) gives

$$\delta E_{n\nu} = C|\omega| \int_0^\infty \mathrm{d}k\, \frac{t^2_{n\nu}(k)}{|\omega| + k} \tag{22}$$

and

$$\delta E_{\nu n} = C|\omega| vp \int_0^\infty \mathrm{d}k\, \frac{t^2_{\nu n}(k)}{|\omega| - k} \tag{23}$$

where

$$C \equiv \frac{1}{4\pi\varepsilon_0} \frac{e^2\hbar^2 2}{\pi m^2 c^2 3}$$

is a constant. Now, we see after the values obtained for $\boldsymbol{T}^{\perp}$ (appendix B) that

$$t^2_{n\nu}(k) = t^2_{\nu n}(k) = \sum_j \frac{a_j}{(h^2 + k^2)^j} \tag{24}$$

(h, a_j constants), where the sum over j is finite. The shift $\delta E_{n\nu}$ is then a sum of integrals of the form

$$\int_0^\infty \frac{\mathrm{d}k}{(|\omega| + k)(1 + h^{-2}k^2)^j} \tag{25}$$

and $\delta E_{\nu n}$ is the same sum, but with the integrals

$$vp \int_0^\infty \frac{\mathrm{d}k}{(|\omega| - k)(1 + h^{-2}k^2)^j} \tag{26}$$

instead of (25). Because $h^{-1} \ll 1$, integrals (25) and (26) have opposite values (appendix F), and equation (21) follows.

(iii) The contribution $\delta E_{n\nu}$, to the shift of level n, of a level ν which is very close to n in energy is negligible. If $E_n < E_\nu$, we have seen that $\delta E_{n\nu}$ is built up of products of the type

$$|\omega| \int_0^\infty \frac{\mathrm{d}k}{(|\omega| + k)(1 + h^{-2}k^2)^j} \tag{27}$$

$$\simeq |\omega| \left[-\log(|\omega| h^{-1}) - \sum_{p=1}^{n-1} \frac{1}{p} \right] \tag{28}$$

(using appendix F), which tend to zero with $|\omega|$. If $E_n > E_\nu$, $\delta E_{\nu n}$ tends to zero with $|\omega|$, then $\delta E_{n\nu}$ also does, because of (21). Therefore, δE_{2s2p} and δE_{3s3p}, for example, are small.

The numerical values of the $\delta E_{n\nu}$ shifts are listed in table 1. For each n, the discrete sum $\sum_\nu \delta E_{n\nu}$ is also given neglecting the high terms ($\nu < 3$p).

The magnetic contribution due to the electron anomalous moment which can be calculated exactly (non-relativistically [2–4] and relativistically [9]) is added to this sum (table 1).

Table 1. Contribution of level ν to the Lamb shift of level n computed from equation (9) (energy unit: $10^{-2}\alpha^5 m_e c^2 = 10^{-2}\alpha^3$ au). Columns: (1–5) values of $\delta E_{n\nu}$; (6) sum of columns (1–5); (7) contribution of the electron anomalous moment to the shift of level n, computed from equation (8); (8) sum of columns 6 and 7; (9) $\Delta E_{AS} - \Delta E_{AP}$ from column (8); (10) experimental value of the Lamb shift, equivalent to the frequencies. $\nu_{2s,2p} = 1058 \times 10^6\ s^{-1}$ (41.3 in units of $10^{-2}\alpha^5 mc^2$) and $\nu_{3s,3p} = 249 \times 10^6\ s^{-1}$ [16, 17].

ν	1s	2s	2p $\parallel$ $\perp$ $\perp$	3s	3p $\parallel$ $\perp$ $\perp$	$\sum_\nu \delta E_{n\nu}$	Contribution electron anomalous moment	(6) + (7)	Difference between states	Experimental difference
n	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
1s	0	0	3.35	0	0.89	12.72	15.91	28.63	—	—
2s	0	0	∼ 0	0	0.14	0.42	1.99	2.41	—	—
									−6.40	± 41.3
			0	—	0.0018	—	—	—	—	—
2p	−3.35	∼ 0	∼ 0	0.014	0.0046	−3.33	−0.66	−3.99	—	—
			∼ 0	—	0.0046	—	—	—	—	—
3s	0	0	−0.014	0	∼ 0	−0.04	0.59	0.55		
									−1.79	± 9.7
			−0.0018	—	0	—	—	—	—	—
3p	−0.89	−0.14	−0.0046	∼ 0	∼ 0	−1.04	−0.20	−1.24	—	—
			−0.0046	—	∼ 0	—	—	—	—	—

4. Calculation of $\delta E_{n\nu}$ for high ν

Because a general expression of $\delta E_{n\nu}$ for any levels $n \equiv (nlm), \nu \equiv (\nu\lambda\mu)$ is difficult to obtain, we restrict the calculation to the case of $n = 1\mathrm{s} \equiv (1,0,0)$ and $\nu = \nu\mathrm{p}_z \equiv (\nu, 1, 0)$.

For $\nu > 1$, equation(1) can be written as

$$\delta E_{1\nu} = -C \int \frac{\mathrm{d}^3 \boldsymbol{k}}{k^2} \frac{\boldsymbol{T}^{\perp}_{\nu n}(\boldsymbol{k}) \cdot \boldsymbol{T}^{\perp}_{n\nu}(\boldsymbol{k})}{\omega + k} \tag{29}$$

where

$$\omega = |\omega_{n\nu}| = \frac{\alpha}{2a}\left(1 - \frac{1}{\nu^2}\right) \tag{30}$$

and

$$C \equiv \frac{e^2 \hbar^2 \omega}{4\pi\varepsilon_0 4\pi^2 m^2 c^2} = \alpha^5 mc^2 \frac{a^2}{8\pi^2}\left(1 - \frac{1}{\nu^2}\right). \tag{31}$$

In order to calculate (29), we use (A3) and the value (G25) of $\boldsymbol{T}^{\perp}$, which give

$$\delta E_{1\nu} = C \frac{12}{(\nu+1)\nu(\nu-1)a^6} 2\pi \int_0^{\pi} \mathrm{d}\beta \sin^3\beta \int_0^{\infty} \frac{\mathrm{d}k}{(\omega+k)k^4} \rho^{2\nu} [\quad]^2 \tag{32}$$

where the square bracket is the same as in (G25). The change of scale $ak \to k$ leads to the final result:

$$\delta E_{1\mathrm{s}\ \nu\mathrm{p}} = \alpha^5 mc^2 \frac{4}{\nu^3 \pi} \int_0^{\infty} \frac{\mathrm{d}k}{k^4(a\omega + k)} \rho^{2\nu} \left[\cos(\nu\theta) + \sin(\nu\theta)\left(-\frac{ah}{\nu k} + \frac{a^2h^2 + k^2}{2k}\right)\right]^2 \tag{33}$$

with the definitions (G25), (30) and

$$\rho^2 \equiv 1 - \frac{4}{\nu(a^2h^2 + k^2)} \tag{34}$$

$$\theta \equiv \tan^{-1} \frac{k}{ah - \frac{1}{2}\nu(a^2h^2 + k^2)} \qquad -\tfrac{1}{2}\pi < \theta \leqslant 0. \tag{35}$$

In (33), the integration over k can be performed numerically by the trapezia method.

For $|\nu\theta| < 5 \times 10^{-2}$ the square bracket in (33) cannot be calculated by a computer, even when double precision is used. In this range, this bracket can be replaced by its second order expansion in θ, which is

$$[\quad] \simeq \frac{\theta^2}{3}(1 - \nu^2). \tag{36}$$

In addition the number of intervals used in the trapezia method is reduced greatly when a logarithmic change of variable is performed on k, that is

$$\int_0^{\infty} f(k)\,\mathrm{d}k = \int_{-\infty}^{\infty} f(k) k\,\mathrm{d}x \tag{37}$$

Table 2. Calculated values of $\delta E_{1s\nu p}$ from equation (33), (energy unit: $10^{-2}\alpha^5 mc^2$), $\int_0^\infty$ represents the integral of equation (33).

ν	$\int_0^\infty$	$\delta E_{1s\nu p}$	ν	$\int_0^\infty$	$\delta E_{1s\nu p}$
2	0.211	3.35	50	0.175	1.78×10^{-4}
3	0.189	0.892	60	0.175	1.03×10^{-4}
4	0.183	0.364	70	0.175	6.50×10^{-5}
5	0.180	0.183	80	0.175	4.35×10^{-5}
6	0.178	0.105	90	0.175	3.06×10^{-5}
7	0.177	6.59×10^{-2}	100	0.175	2.23×10^{-5}
8	0.177	4.40×10^{-2}	150	0.175	6.60×10^{-6}
9	0.176	3.08×10^{-2}	200	0.175	2.78×10^{-6}
10	0.176	2.24×10^{-2}	300	0.175	8.25×10^{-7}
20	0.175	2.79×10^{-3}	500	0.175	1.78×10^{-7}
30	0.175	8.26×10^{-4}	1000	0.175	2.23×10^{-8}
40	0.175	3.48×10^{-4}	2000	0.175	2.78×10^{-9}

with $k = \exp x$.

Examples of calculated values of $\delta E_{1s\nu p}$ are given in table 2. For fixed k, we have in (33) the limits

$$\rho^{2\nu} \sim \exp \frac{-4}{1+k^2} \tag{38}$$

and

$$\begin{cases} [\quad] \sim \cos\gamma - \frac{1}{\gamma}\sin\gamma \\ \gamma \equiv -2k/(1+k^2) \end{cases} \tag{39}$$

when ν tends to infinity. In practice, the integral $\int_0^\infty$ in (33) can be replaced by its asymptotic value

$$\int_0^\infty \frac{\mathrm{d}k}{k^4(a\omega + k)} \exp \frac{-4}{1+k^2} \left[\cos\gamma - \frac{1}{\gamma}\sin\gamma\right]^2 = 0.175 \tag{40}$$

for $\nu > 9$. This leads to the approximation

$$\delta E_{1s\nu p} \simeq \alpha^5 mc^2 \frac{0.700}{\nu^3 \pi} \qquad \nu > 8. \tag{41}$$

The contribution of all p levels to the shift of the 1s level can be obtained using table 2 and the approximation (41):

$$\sum_{\nu=2}^{\infty} \delta E_{1s\nu p} = 3\left[\sum_{\nu=2}^{9} + \sum_{\nu=10}^{\infty}\right] \tag{42}$$

$$= 3\left[5.03 + \frac{70}{\pi}\sum_{\nu=10}^{\infty}\frac{1}{\nu^3}\right]$$

$$= 15.45 \qquad \text{(in energy units : } 10^{-2}\alpha^5 mc^2\text{)}. \tag{43}$$

To obtain (43), the value $\zeta(3) = 1.20$ for the Riemann ζ function has been used.

5. Conclusions

As shown in columus (9) and (10) of table 1, the contributions of the discrete levels $\delta E_{n\nu}$ as given by formula (9) are only a small part (15–20%) of the whole shift. This result is in agreement with the previous results obtained using equation (4) [5, 3].

Expressions (9) and (4) will now be compared directly for a few (n, ν) levels. Clearly, this comparison is a little problematic because (9) is well defined whereas (4) depends strongly on the value given to λ. In Bethe's computation of the *total shift* (6) + (7) + (8), the precise value of λ is not needed. This is due to the fact that the part of (4) which depends on λ, that is the first term in (6), is cancelled by the first term in (7), and therefore does not need to be calculated.

In contrast, if we want to use (4) instead of (9) for individual contributions, then a precise value needs to be given to λ in (7), since a compensating term in λ will no longer appear in W_2. Work is in progress to obtain a λ-independent expression for W_4 in the framework of self-energy electrodynamics.

For a rough numerical comparison of (9) and (4) we shall choose in (4) the minimum cut-off value

$$\lambda c = \alpha mc^2 = \frac{\hbar}{a} c \tag{44}$$

(correspondingly, the first logarithm in (7) must be set equal to $-\ln\alpha$). The values drawn from (9) and (4) are compared for levels $(n, \nu) =$ (1s, 2p), (1s, 3p) and (2s, 3p) (table 3). The difference of approximately 5% may induce in the total Lamb shift (6) + (7) + (8) a difference of approximately 5% × 15% = 1%. Because of approximation (44) made in (7), this difference may vary and will not be discussed further here.

Table 3. Contribution of level ν to the shift of level n: comparison of expressions (9) and (4) (in which λ is given by (44)). Units: $10^{-2}\alpha^5 mc^2$.

(n, ν)	(1s,2p)	(1s,3p)	(2s,3p)
Equation (9)	3.35	0.89	0.14
Equation (4)	3.66	0.95	0.17
Difference	3%	5%	18%

As emphasized earlier, the use of equation (9) for precise calculations, in place of equation (4), now *rests* on obtaining an exact expression for the high energy term W_4.

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Appendix A. Calculation of integrals

$$\boldsymbol{T}^{\perp}_{\nu n}(\boldsymbol{k}) \equiv \left[\int \mathrm{d}^3\boldsymbol{x}\ \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}\,\psi_\nu(\boldsymbol{x})\nabla\psi_n(\boldsymbol{x})\right]^{\perp} \tag{A1}$$

where $\perp$ indicates that only the component of $\boldsymbol{T}$ orthogonal to $\boldsymbol{k}$ is taken.

A.1. Effects of permutation of indexes

$\boldsymbol{T}_{\nu n}$ satisfies

$$\boldsymbol{T}_{\nu n}(\boldsymbol{k}) = -\boldsymbol{T}_{n\nu}(\boldsymbol{k}) - \mathrm{i}\boldsymbol{k}I_{\nu n}(-\boldsymbol{k}) \tag{A2}$$

where $I_{\nu n}$ is defined by

$$I_{\nu n}(\boldsymbol{k}) \equiv \int \mathrm{d}^3\boldsymbol{x}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \psi_\nu(\boldsymbol{x})\psi_n(\boldsymbol{x}). \tag{A3}$$

Therefore we have

$$\boldsymbol{T}^{\perp}_{\nu n}(\boldsymbol{k}) = -\boldsymbol{T}^{\perp}_{n\nu}(\boldsymbol{k}). \tag{A4}$$

A.2. Effect of reversion of $\boldsymbol{k}$

$\boldsymbol{T}^{\perp}(-\boldsymbol{k})$ occurs in (1). Here the orbitals ψ_n, ψ_ν are taken to be real. Therefore, $\boldsymbol{T}(\boldsymbol{k})$ and $\boldsymbol{T}(-\boldsymbol{k})$ are conjugate. The same holds for $\boldsymbol{T}^{\perp}$. $\boldsymbol{T}^{\perp}_{1\mathrm{s}2\mathrm{p}}, \boldsymbol{T}^{\perp}_{1\mathrm{s}3\mathrm{p}}, \boldsymbol{T}^{\perp}_{2\mathrm{s}2\mathrm{p}}, \boldsymbol{T}^{\perp}_{2\mathrm{s}3\mathrm{p}}$ and $\boldsymbol{T}^{\perp}_{3\mathrm{s}2\mathrm{p}}$ happen to be real, and therefore they verify

$$\boldsymbol{T}^{\perp}(-\boldsymbol{k}) = \boldsymbol{T}^{\perp}(\boldsymbol{k}) \tag{A5}$$

whereas $\boldsymbol{T}^{\perp}_{2\mathrm{p}\ 3\mathrm{p}}$ which is imaginary verifies

$$\boldsymbol{T}^{\perp}(-\boldsymbol{k}) = -\boldsymbol{T}^{\perp}(\boldsymbol{k}). \tag{A6}$$

A.3. General formula for $\boldsymbol{T}^{\perp}_{\nu n}$

The Bohr radius a will be taken to be unity ($a = 1$) in orbitals ψ_ν and ψ_n. This is possible provided the final result for $\boldsymbol{T}^{\perp}$ is multiplied by a^{-1}, and that $\boldsymbol{k}$ is replaced by $a\boldsymbol{k}$. The hydrogen orbitals are then taken in the form [14]

$$\psi_n \equiv \psi_{nlm}(r,\theta',\varphi') = N_{nl}F_{nl}\left(\frac{2r}{n}\right) C_{lm} P_l^m(\cos\theta') \begin{matrix}\cos\\ \sin\end{matrix}(m\varphi') \tag{A7}$$

with

$$F_{nl}(x) \equiv x^l \mathrm{e}^{-x/2} L^{2l+1}_{n-l-1}(x) \tag{A8}$$

$$N_{nl} \equiv \frac{2}{n^2}\left[\frac{(n-l-1)!}{(n+l)!^3}\right]^{1/2} \tag{A9}$$

$$C_{lm} \equiv (-1)^m \left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}2^{\varepsilon(m)}\right]^{1/2} \tag{A10}$$

$$\varepsilon(m) = 0 \text{ (for } m = 0) \qquad \text{or} \qquad 1 \text{ (for } m \neq 0).$$

The Laguerre polynomials L are normalized as in [14]. The spherical coordinates (r,θ',φ') refer to an axis of symmetry e_3 of ψ_n.

The gradient of ψ_n is

$$\nabla\psi_{nlm} = N_{nl}C_{lm}\left[P_l^m(\cos\theta')\frac{\cos}{\sin}(m\varphi')\nabla F_{nl}\left(\frac{2r}{n}\right)\right.$$
$$\left. + F_{nl}\left(\frac{2r}{n}\right)\left[\nabla(P_l^m(\cos\theta'))\frac{\cos}{\sin}(m\varphi') + P_l^m(\cos\theta')\nabla\frac{\cos}{\sin}(m\varphi')\right]\right] \tag{A11}$$

with

$$\nabla F_{nl}\left(\frac{2r}{n}\right) = \boldsymbol{u}\frac{2}{n}x^l\mathrm{e}^{-x/2}\left[L_N^\Lambda(x)\left(\frac{l}{x}-\frac{1}{2}\right) - L_{N-1}^{\Lambda+1}(x)\right] \tag{A12}$$

$(N \equiv n-l-1; \Lambda \equiv 2l+1; x \equiv 2r/n; \boldsymbol{u} \equiv \boldsymbol{r}/r)$. Here we have used $(\partial/\partial z)L_p^k = -L_{p-1}^{k+1}$. (see [12]). In (A11) we have also

$$\nabla P_l^m(\cos\theta') = \frac{\mathrm{d}P_l^m(\cos\theta')}{\mathrm{d}\cos\theta'}\frac{1}{r}(\boldsymbol{e}_3 - \boldsymbol{u}\cos\theta') \tag{A13}$$

and

$$\nabla\frac{\cos}{\sin}(m\varphi') = \frac{m}{r\sin^2\theta'}\boldsymbol{e}_3\wedge\boldsymbol{u}\frac{-\sin}{\cos}(m\varphi'). \tag{A14}$$

To take the component of $\nabla\psi_n$ orthogonal to $\boldsymbol{k}$, we shall use two frames: the spherical coordinates (r,θ,φ) are associated with frame $(\boldsymbol{i},\boldsymbol{j},\boldsymbol{k}/|\boldsymbol{k}|)$; and the spherical coordiantes (r,θ',φ') with frame $(\boldsymbol{i},\boldsymbol{j}',\boldsymbol{e}_3)$.

In (A12), $\boldsymbol{u}$ must be replaced by its component orthogonal to $\boldsymbol{k}$,

$$\boldsymbol{u}^\perp = \sin\theta\sin\varphi\boldsymbol{j}. \tag{A15}$$

In (A13), we must substitute

$$(\boldsymbol{e}_3 - \boldsymbol{u}\cos\theta')^\perp = \boldsymbol{j}(\sin\beta - \cos\theta'\sin\theta\sin\varphi) \tag{A16}$$

and in (A14)

$$(\boldsymbol{e}_3\wedge\boldsymbol{u})^\perp = \sin\theta\cos\varphi\cos\beta\ \boldsymbol{j}. \tag{A17}$$

Then we obtain

$$\left[\nabla\left\{F_{nl}\left(\frac{2r}{n}\right)P_l^m(\cos\theta')\frac{\cos}{\sin}(m\varphi')\right\}\right]^\perp$$
$$= \boldsymbol{j}\left(\frac{2r}{n}\right)^l\mathrm{e}^{-r/n}\frac{1}{r}\left\{L_{n-l-1}^{2l+1}\left(\frac{2r}{n}\right)\left[\frac{1}{n}(\ln - r)\sin\theta\sin\varphi P_l^m(\cos\theta')\frac{\cos}{\sin}(m\varphi')\right.\right.$$
$$+\frac{\mathrm{d}P_l^m(\cos\theta')}{\mathrm{d}\cos\theta'}(\sin\beta - \cos\theta'\sin\theta\sin\varphi)\frac{\cos}{\sin}(m\varphi')$$
$$\left.+P_l^m(\cos\theta')\frac{m}{\sin^2\theta'}\sin\theta\cos\varphi\cos\beta\frac{-\sin}{\cos}(m\varphi')\right]$$
$$\left.-\frac{2}{n}rL_{n-l-2}^{2l+2}\left(\frac{2r}{n}\right)\sin\theta\sin\varphi\ P_l^m(\cos\theta')\frac{\cos}{\sin}(m\varphi')\right\}. \tag{A18}$$

Substitution of (A18) for $(\nabla\psi_n)^\perp$ in (A6) gives the final result

$$T^\perp_{\nu n} = j N_{\nu\lambda} N_{nl} C_{\lambda\mu} C_{lm} \frac{2^{\lambda+l}}{\nu^\lambda n^l} \int_{r=0}^{\infty} \mathrm{d}r\, r^{\lambda+l+1} \mathrm{e}^{-r(1/\nu+1/n)} L^{2\lambda+1}_{\nu-\lambda-1}\left(\frac{2r}{\nu}\right)$$
$$\times \left\{ L^{2l+1}_{n-l-1}\left(\frac{2r}{n}\right)\left[\frac{1}{n}(\ln - r)\,{}^{1}\!\!\int_\theta + {}^{2}\!\!\int_\theta + m\cos\beta\,{}^{3}\!\!\int_\theta\right] - \frac{2}{n} r L^{2l+2}_{n-l-2}\left(\frac{2r}{n}\right){}^{1}\!\!\int_\theta \right\} \tag{A19}$$

where

$${}^{1}\!\!\int_\theta \equiv \int_{\theta=0}^{\pi} \mathrm{d}\theta \sin^2\theta\, \mathrm{e}^{\mathrm{i}kr\cos\theta} \int_{\varphi=0}^{2\pi} \mathrm{d}\varphi \sin\varphi\, P^\mu_\lambda(\cos\theta') P^m_l(\cos\theta') \begin{matrix}\cos\\ \sin\end{matrix}(\mu\varphi') \begin{matrix}\cos\\ \sin\end{matrix}(m\varphi') \tag{A20}$$

$${}^{2}\!\!\int_\theta \equiv \int_{\theta=0}^{\pi} \mathrm{d}\theta \sin\theta\, \mathrm{e}^{\mathrm{i}kr\cos\theta} \int_{\varphi=0}^{2\pi} \mathrm{d}\varphi P^\mu_\lambda(\cos\theta') \frac{\mathrm{d}P^m_l(\cos\theta')}{\mathrm{d}\cos\theta'} (\sin\beta - \cos\theta' \sin\theta \sin\varphi) \begin{matrix}\cos\\ \sin\end{matrix}(\mu\varphi') \begin{matrix}\cos\\ \sin\end{matrix}(m\varphi') \tag{A21}$$

$${}^{3}\!\!\int_\theta \equiv \int_{\theta=0}^{\pi} \mathrm{d}\theta \sin^2\theta\, \mathrm{e}^{\mathrm{i}kr\cos\theta} \int_{\varphi=0}^{2\pi} \mathrm{d}\varphi \cos\varphi \frac{P^\mu_\lambda(\cos\theta') P^m_l(\cos\theta')}{\sin^2\theta'} \begin{matrix}\cos\\ \sin\end{matrix}(\mu\varphi') \begin{matrix}-\sin\\ \cos\end{matrix}(m\varphi'). \tag{A22}$$

A.4. Calculation of integrals ${}^1\!\int_\theta, {}^2\!\int_\theta, {}^3\!\int_\theta$ *for low values of quantum numbers* λ, μ *and* l, m

We notice that only the last quantum numbers λ, μ and l, m of the orbitals $\nu \equiv (\nu\lambda\mu)$ and $n \equiv (nlm)$ are involved in (A21)–(A22) and thanks to relationship (A4), we may assume $l \leqslant \lambda$, and $m \leqslant \mu$ for $l = \lambda$.

The integrals over φ occurring in ${}^1\!\int_\theta, {}^2\!\int_\theta, {}^3\!\int_\theta$ respectively, are denoted by ${}^1\!\int_\varphi, {}^2\!\int_\varphi, {}^3\!\int_\varphi$. For integration of (A21)–(A22), coordinates (r, θ', φ') are expressed as functions of (r, θ, φ), using relationships like

$$\cos\varphi' = \sin\theta\cos\varphi / \sin\theta' \tag{A23}$$

and

$$\sin\varphi' = (-\cos\theta\sin\beta + \sin\theta\sin\varphi\cos\beta)/\sin\theta'. \tag{A24}$$

(a) $\lambda = 0, l = 0$ (two s orbitals). Then

$${}^{1}\!\!\int_\theta = 0 = {}^{2}\!\!\int_\theta \qquad \text{and} \qquad m\,{}^{3}\!\!\int_\theta = 0. \tag{A25}$$

(b) $\lambda = 1, \mu = 0; l = 0$ (p_z and s orbitals).

$$\overset{1}{\int}_{\varphi} = \pi \sin\beta \sin\theta$$

$$\overset{1}{\int}_{\theta} = \pi \sin\beta\ \Theta_{30}(kr) \qquad \text{(for } \Theta_{mn}\text{, see appendix C)}$$

$$\overset{2}{\int}_{\theta} = 0 \qquad m\overset{3}{\int}_{\theta} = 0. \tag{A26}$$

(c) $\lambda = 1, \mu = 0; l = 1, m = 0$ (two p orbitals with the same axis).

$$\overset{1}{\int}_{\varphi} = 2\pi \sin\beta \cos\beta \sin\theta \cos\theta$$

$$\overset{1}{\int}_{\theta} = \pi \sin(2\beta)\ \Theta_{31}(kr)$$

$$\overset{2}{\int}_{\varphi} = \pi \sin(2\beta) \cos^3\theta$$

$$\overset{2}{\int}_{\theta} = \pi \sin(2\beta)\ \Theta_{13}(kr)$$

$$m\overset{3}{\int}_{\theta} = 0. \tag{A27}$$

(d) $\lambda = 1, \mu = \pm 1; l = 0$ (orbitals p_x (or p_y) and s). This case will give the same value of $\boldsymbol{T}^{\perp}$ as case (b) above

(e) $\lambda = 1, \mu = 1; l = 1, m = 0$ (p_x and p_z orbitals). The axis $\boldsymbol{e}_3$ of the (l, m) orbital has any orientation; the (λ, μ) orbital is assumed to be orthogonal to both $\boldsymbol{k}$ and $\boldsymbol{e}_3$ (axis $\boldsymbol{e}_3 \times \boldsymbol{k}$).

$$\overset{1}{\int}_{\theta} = 0 = \overset{2}{\int}_{\theta} \qquad m\overset{3}{\int}_{\theta} = 0. \tag{A28}$$

(f) $\lambda = 1, \mu = -1; l = 1, m = 0$ (p_y and p_z orbitals). The axis $\boldsymbol{e}_3$ of the (l, m) orbital has any orientation; the (λ, μ) orbital is assumed to be orthogonal to $\boldsymbol{e}_3$, and coplanar with $\boldsymbol{e}_3$ and $\boldsymbol{k}$ (axis $\boldsymbol{j}'$).

$$\overset{1}{\int}_{\varphi} = \pi \cos(2\beta) \sin\theta \cos\theta$$

$$\overset{1}{\int}_{\theta} = \pi \cos(2\beta)\ \Theta_{31}(kr)$$

$$\overset{2}{\int}_{\varphi} = -\pi(2\sin^2\beta \cos\theta + \cos(2\beta) \sin^2\theta \cos\theta)$$

$$\overset{2}{\int}_{\theta} = -\pi[2\sin^2\beta\ \Theta_{11}(kr) + \cos(2\beta)\ \Theta_{31}(kr)]$$

$$m\overset{3}{\int}_{\theta} = 0. \tag{A29}$$

(g) $\lambda = 1, \mu = \pm 1; l = 1, m = \mp 1$ (p_x and p_y orbitals). $\boldsymbol{T}^{\perp} = 0$ as in case (e) above.

(h) $\lambda = 1, \mu = \pm 1; l = 1, m = \pm 1$ (two p_x or two p_y orbitals). Same case as (c) above.

(i) $\lambda = 2, \mu = 0; l = 0$ (d_{zz} and s orbitals).

$$ {}^1\!\!\int_{\varphi} = \frac{3\pi}{2} \sin(2\beta) \sin\theta \cos\theta $$

$$ {}^1\!\!\int_{\theta} = \frac{3\pi}{2} \sin(2\beta)\ \Theta_{31}(kr) $$

etc.

Appendix B. Explicit expression of $T^{\perp}_{\nu n}(k)$ (as defined by (A6)) for ν, n= 1s, 2s, 2p, 3s, 3p

(a) $\boldsymbol{T}^{\perp}_{\nu s n s}$ (two s orbitals). By symmetry, $\boldsymbol{T}_{\nu s n s}$ is parallel to $\boldsymbol{k}$. Therefore for any s orbitals νs and ns we have for any value of $\boldsymbol{k}$

$$ \boldsymbol{T}^{\perp}_{\nu s n s}(\boldsymbol{k}) = 0. \tag{B1} $$

(b) $\boldsymbol{T}^{\perp}_{\nu p_x n p_z}$ (two p orbitals with perpendicular axes). For the special values of $\boldsymbol{k}$ perpendicular to one or the other of the orbitals axes, we have

$$ \boldsymbol{T}^{\perp}_{\nu p_x n p_z}(\boldsymbol{k}) = 0 \qquad (\boldsymbol{k} \perp \boldsymbol{e}_3 \text{ or } \boldsymbol{e}_0). \tag{B2a} $$

This is a consequence of (A28).

(c) Expression of $\boldsymbol{T}^{\perp}_{2p1s}(\boldsymbol{k})$. For $\nu \equiv (\nu\lambda\nu) = (2,1,0)$ and $n \equiv (nlm) = (1,0,0)$, (A19) is written

$$ \boldsymbol{T}^{\perp} = -\frac{\boldsymbol{j}}{4\sqrt{2}} \sin\beta \int_0^{\infty} \mathrm{d}r\, r^3 \mathrm{e}^{-3r/2} \Theta_{30}(kr). \tag{B2b} $$

(B2a) is obtained using definitions (A9) and (A10) and ${}^1\!\!\int_{\theta}, {}^2\!\!\int_{\theta}, {}^3\!\!\int_{\theta}$ as given by (A26). The unit vector $\boldsymbol{j}$ is bound to $\boldsymbol{k}$ and to the axis $\boldsymbol{e}_3$ of the 2p orbital, as defined in section 2 or appendix A. Substitution of (C6) in (B2) leads to

$$ \boldsymbol{T}^{\perp} = \frac{\boldsymbol{j} \sin\beta}{\sqrt{2} k^2} \left[C_1(h,k) - \frac{1}{k} S_0(h,k) \right] \qquad (h \equiv \tfrac{3}{2}) \tag{B3} $$

with C_1 and S_0 defined by (D1) and (D2). Substitution of (D5), (D8) and reinsertion of the Bohr radius a as explained in appendix A, finally leads to

$$ \boldsymbol{T}^{\perp}_{2p1s} = -\frac{\sqrt{2} \boldsymbol{j} \sin\beta}{a^5 (h^2 + k^2)^2} \tag{B4} $$

($h \equiv 3/2a; \beta \equiv$ angle $(\boldsymbol{k}, \boldsymbol{e}_e)$).

(d) $T^{\perp}_{2p2s}((\nu\lambda\mu) = (2,1,0)$ and $(nlm) = (2,0,0))$. Substitution of (A26), (A9) and (A10) into (A19) gives

$$T^{\perp} = \frac{j \sin\beta}{64} \int_0^{\infty} \mathrm{d}r \, \mathrm{e}^{-r} r^3 (4 - r) \, \Theta_{30}(kr). \tag{B5}$$

Successive use of (C6), (D5), (D6), (D8) and (D9) leads to

$$T^{\perp}_{2p2s} = \frac{j \sin\beta}{2a^5} \left[-\frac{1}{(h^2 + k^2)^2} + \frac{1}{a^2(h^2 + k^2)^3} \right] \tag{B6}$$

$(h \equiv 1/a)$, after reinsertion of the Bohr radius a.

(e) $T^{\perp}_{2p3s}((\nu\lambda\mu) = (2,1,0)$ and $(nlm) = (3,0,0))$. Substitution of (A26), (A4) and (A5) into (A19) gives

$$T^{\perp} = \frac{j \sin\beta}{4 \times 81\sqrt{6}} \int_0^{\infty} \mathrm{d}r \, \mathrm{e}^{-5r/6} r^3 (-27 + 10r - \tfrac{2}{3} r^2) \Theta_{30}(kr). \tag{B7}$$

Successive use of (C6) and (D5)–(D10) leads to

$$T^{\perp}_{2p3s} = j \frac{2 \sin\beta}{81\sqrt{6} a^5 (h^2 + k^2)^2} \left[-27 + \frac{4}{a^2} \frac{9k^2 + 5h^2}{(h^2 + k^2)^2} \right] \tag{B8}$$

$(h \equiv 5/6a)$, after reinsertion of the Bohr radius a.

(f) $T^{\perp}_{3p1s}((\nu\lambda\mu) = (3,1,0)$ and $(nlm) = (1,0,0))$. Substitution of (A26), (A9) and (A10) into (A19) gives

$$T^{\perp} = j \sin\beta \frac{\sqrt{2}}{81} \int_0^{\infty} \mathrm{d}r \, \mathrm{e}^{-4r/3} r^3 (r - 6) \Theta_{30}(kr). \tag{B9}$$

Successive use of (C6), (D5), (D6), (D8) and (D9) leads to

$$T^{\perp}_{3p1s} = j \sin\beta \frac{16\sqrt{2}}{81a^5} \frac{1}{(h^2 + k^2)^2} \left[\frac{2h}{a(h^2 + k^2)} - 3 \right] \tag{B10}$$

$(h \equiv 4/3a)$, after reinsertion of a.

(g) $T^{\perp}_{3p2s}((\nu\lambda\mu) = (3,1,0)$ and $(nlm) = (2,0,0))$. Substitution of (A26), (A9) and (A10) into (A19) gives

$$T^{\perp} = \frac{j \sin\beta}{4 \times 81} \int_0^{\infty} \mathrm{d}r \, \mathrm{e}^{-5r/6} r^3 (6 - r) \left(-2 + \frac{r}{2} \right) \Theta_{30}(kr). \tag{B11}$$

Successive use of (C6) and (D5)–(D10) leads to

$$T^{\perp}_{3p2s} = j \sin\beta \frac{4}{81a^5} \frac{1}{(h^2 + k^2)^2} \left[-6 + \frac{28}{3a^2(h^2 + k^2)} - \frac{25}{6a^4(h^2 + k^2)^2} \right] \tag{B12}$$

$(h \equiv 5/6a)$, after reinsertion of a.

(h) $\boldsymbol{T}_{3p_z,2p_z}((\nu\lambda\mu)=(3,1,0)$ and $(nlm)=(2,1,0))$. Substitution of (A27), (A9) and (A10) into (A19) gives

$$\boldsymbol{T}^{\perp}=\frac{\boldsymbol{j}\sin(2\beta)}{2^3 3^4}\int_0^\infty \mathrm{d}r\,\mathrm{e}^{-5r/6}r^3(6-r)[(2-r)\Theta_{31}(kr)+2\Theta_{13}(kr)]. \tag{B13}$$

Successive use of (C3), (C7), (C8) and (D5)–(D10) leads to

$$\boldsymbol{T}^{\perp}_{3p_z,2p_z}(\boldsymbol{k})=\mathrm{i}\boldsymbol{j}\sin(2\beta)\frac{10}{3^5a^8}\frac{k}{(h^2+k^2)^4} \tag{B14}$$

$(h\equiv 5/6a)$. (B14) is valid for any orientation of $\boldsymbol{k}$ with respect to the common symmetry axis of the orbitals. $\boldsymbol{T}^{\perp}$ is an imaginary vector.

(i) $\boldsymbol{T}^{\perp}_{3p_y,2p_z}((\nu\lambda\mu)=(3,1,-1)$ and $(nlm)=(2,1,0))$. In the case of two orbitals whose symmetry axes $\boldsymbol{e}_0$ and $\boldsymbol{e}_3$ are perpendicular, we need only the value of $\boldsymbol{T}^{\perp}(\boldsymbol{k})$ for special orientations of $\boldsymbol{k}$ (see section 2).

When $\boldsymbol{k}$ is perpendicular to either one of the axes, we know that $\boldsymbol{T}^{\perp}(\boldsymbol{k})$ is zero (see (B2)).

We now consider the case where $\boldsymbol{k}$ is coplanar with $\boldsymbol{e}_0$ and $\boldsymbol{e}_3$. The $\boldsymbol{e}_0$ axis of the 3p orbital is therefore chosen on the $\boldsymbol{j}'$ axis.

Substitution of (A29), (A9) and (A10) in (A19) gives

$$\boldsymbol{T}^{\perp}=\frac{\boldsymbol{j}}{3^4 2^3}\left[\cos(2\beta)\int_0^\infty \mathrm{d}r\,\mathrm{e}^{-5r/6}r^4(6-r)\Theta_{31}(kr)\right.$$
$$\left.+4\sin^2\beta\int_0^\infty \mathrm{d}r\,\mathrm{e}^{-5r/6}r^3(6-r)\Theta_{11}(kr)\right]. \tag{B15}$$

Successive use of (C3), (C7), (D5) and (D11) leads to

$$\boldsymbol{T}^{\perp}_{3p_y,2p_z}(\boldsymbol{k})=\mathrm{i}\boldsymbol{j}\frac{2^3k}{3^3a^6(h^2+k^2)^3}\left[\cos(2\beta)\left(1-\frac{5}{6a^2(h^2+k^2)}\right)\right.$$
$$\left.+2\sin^2\beta\left(1-\frac{25}{36a^2(h^2+k^2)}\right)\right] \tag{B16}$$

$(h\equiv 5/6a)$, *after reinsertion of* a. (B16) is valid only for $\boldsymbol{k}$ belonging to the yz plane. $\boldsymbol{T}^{\perp}$ is then imaginary.

Appendix C. Evaluation of the integral

$$\Theta_{mn}\equiv\int_0^\pi \mathrm{d}\theta\,\sin^m\theta\cos^n\theta\,\mathrm{e}^{\mathrm{i}r\cos\theta} \tag{C1}$$

for some small values of integers m,n (r real).

We have

$$\Theta_{10} = \frac{2}{r}\sin r (C.2)$$

$$\Theta_{11} = \frac{2i}{r}\left(-\cos r + \frac{1}{r}\sin r\right) \tag{C3}$$

$$\Theta_{12} = \frac{2}{r}\left[\frac{2}{r}\cos r + \left(1 - \frac{2}{r^2}\right)\sin r\right] \tag{C4}$$

$$\Theta_{13} = i\frac{2}{r}\left[\left(-1 + \frac{6}{r^2}\right)\cos r + \left(\frac{3}{r} - \frac{6}{r^3}\right)\sin r\right] \tag{C5}$$

$$\Theta_{30} = \frac{4}{r^2}\left(-\cos r + \frac{1}{r}\sin r\right) \tag{C6}$$

$$\Theta_{31} = i\frac{4}{r^2}\left[-\frac{3}{r}\cos r + \left(-1 + \frac{3}{r^2}\right)\sin r\right]. \tag{C7}$$

The relationship

$$\Theta_{mn} = \Theta_{m+2,n} + \Theta_{m,n+2} \tag{C8}$$

is useful.

Appendix D. Values or majoration of the integrals

$$C_n(h,k) = \int_0^\infty \mathrm{d}x\, x^n\, \mathrm{e}^{-hx}\cos(kx) \tag{D1}$$

and

$$S_n(h,k) = \int_0^\infty \mathrm{d}x\, x^n\, \mathrm{e}^{-hx}\sin(kx) \tag{D2}$$

(i) For $\mathrm{Re}\, h > 0$ and $k > 0$, we have [15]

$$C_n = n!\left(\frac{h}{h^2+k^2}\right)^{n+1} \sum_{0\leqslant 2p\leqslant n+1} (-1)^p \binom{n+1}{2p}\left(\frac{k}{h}\right)^{2p} \tag{D3}$$

and

$$S_n = n!\left(\frac{h}{h^2+k^2}\right)^{n+1} \sum_{0\leqslant 2p\leqslant n} (-1)^p \binom{n+1}{2p+1}\left(\frac{k}{h}\right)^{2p+1} \tag{D4}$$

For $n = 0, 1, 2, 3$, (D3) or (D4) gives

$$C_1 = (h^2 - k^2)/H^2 \qquad (H \equiv h^2 + k^2) \tag{D5}$$

$$C_2 = 2h(h^2 - 3k^2)/H^3 \tag{D6}$$

$$C_3 = 6(h^4 + k^4 - 6h^2k^2)/H^4 \tag{D7}$$

$$S_0 = k/H \tag{D8}$$

$$S_1 = 2hk/H^2 \tag{D9}$$

$$S_2 = -2k(k^2 - 3h^2)/H^3 \tag{D10}$$

$$S_3 = 24hk(h^2 - k^2)/H^4. \tag{D11}$$

We also have [15]

$$\begin{matrix} C_n \\ S_n \end{matrix} = \frac{\Gamma(n+1)}{(h^2+k^2)^{(n+1)/2}} \begin{matrix} \sin \\ \cos \end{matrix} \left[(n+1)\tan^{-1}\frac{k}{h}\right] \tag{D12}$$

and therefore

$$\left|\begin{matrix} C_n \\ S_n \end{matrix}\right| \leqslant \frac{n!}{(h^2+k^2)^{(n+1)/2}}. \tag{D13}$$

(ii) Majoration of $|C_n - k^{-1}S_{n-1}|$. Other expressions of C_n and S_n are [15]

$$S_n = (-1)^n \frac{\partial^n}{\partial h^n} \frac{k}{k^2+h^2} \tag{D14}$$

$$C_n = (-1)^n \frac{\partial^n}{\partial h^n} \frac{h}{k^2+h^2}. \tag{D15}$$

Hence,

$$C_n - \frac{1}{k}S_{n-1} = (-1)^n 2k^2 \frac{\partial^{n-1}}{\partial h^{n-1}} \frac{1}{(h^2+k^2)^2}. \tag{D16}$$

To majorate the derivative in (D16),

$$\frac{\partial^n}{\partial h^n}\frac{1}{(h^2+k^2)^n} = \sum_{s=0}^{n} \binom{n}{s} \frac{\partial^s}{\partial h^s}\left(\frac{1}{h^2+k^2}\right) \frac{\partial^{n-s}}{\partial h^{n-s}} \frac{1}{h^2+k^2} \tag{D17}$$

let us use the inequality

$$\left|\frac{\partial^s}{\partial h^s}\frac{1}{h^2+k^2}\right| \leqslant \frac{1}{k}\frac{s!}{(h^2+k^2)^{(s+1)/2}} \tag{D18}$$

which is a consequence of (D14) and (D12). We obtain

$$\left|\frac{\partial^n}{\partial h^n}\frac{1}{(h^2+k^2)^2}\right| \leqslant \frac{(n+1)!}{k^2(h^2+k^2)^{(n+2)/2}}. \tag{D19}$$

Substitution of (D19) into (D16) yields

$$\left|C_n - \frac{1}{k}S_{n-1}\right| \leqslant 2\frac{n!}{(h^2+k^2)^{(n+1)/2}}. \tag{D20}$$

Another majoration of $|C_n - 1/kS_{n-1}|$ will be found now, thanks to another majoration of the derivative in (D16).

$$\frac{\partial^n}{\partial h^n}\frac{1}{(h^2+k^2)^n} = \sum_{s=0}^{n}\binom{n}{s}\frac{\partial^s}{\partial h^s}\frac{1}{(h+\mathrm{i}k)^2}\frac{\partial^{n-s}}{\partial h^{n-s}}\frac{1}{(h-\mathrm{i}k)^2} \tag{D21}$$

$$= (-1)^n\frac{n!}{(h^2+k^2)^2(h-\mathrm{i}k)^n}\sum_{s=0}^{n}(s+1)(n-s+1)\left(\frac{h-\mathrm{i}k}{h+\mathrm{i}k}\right)^s \tag{D22}$$

$$\left|\sum_{s=0}^{n}\right| \leqslant \sum_{s=0}^{n}(s+1)(n-s+1) = (n+1)(n+2)(n+3)/6. \tag{D23}$$

(D16), (D22) and (D23) lead to

$$\left|C_n - \frac{1}{k}S_{n-1}\right| \leqslant k^2\frac{(n+2)!}{3(h^2+k^2)^{(n+3)/2}}. \tag{D24}$$

Appendix E. Calculation of the shifts $\delta E_{n\nu}$ for levels $n,\nu = 1s, 2s, 2p, 3s, 3p$

(a) $n = 1\mathrm{s}, \nu = 2\mathrm{p}$. After (B4), $T^{\perp}_{2\mathrm{p}1\mathrm{s}}$ is of the form (13) with

$$t_{21}(\boldsymbol{k}) \equiv -\frac{\sqrt{2}}{a^5(h^2+k^2)^2} \qquad \left(h \equiv \frac{3}{2a}\right). \tag{E1}$$

In (9), the integral over $\boldsymbol{k}$ is given by (14*a*) and (A4) and (A5):

$$\int_{\boldsymbol{k}} = 2\pi\left(\int_0^{\pi}\mathrm{d}\beta\sin^3\beta\right)\int_0^{\infty}\mathrm{d}k\,\frac{-t_{21}^2(k)}{\omega_{12}-k}. \tag{E2}$$

Using

$$\omega_{12} = -\frac{\alpha}{2a}\left(\frac{1}{n^2}-\frac{1}{\nu^2}\right) = -\frac{3\alpha}{8a} \qquad \left(\alpha \equiv \frac{1}{4\pi\varepsilon_0}\frac{\mathrm{e}^2}{\hbar c}\right) \tag{E3}$$

and (E1) and (E2) in (9), we obtain

$$\frac{\delta E_{1\mathrm{s}2\mathrm{p}}}{\alpha^5 mc^2} = \frac{1}{2\pi a^8}\int_0^{\infty}\frac{\mathrm{d}k}{(3\alpha/8a+k)\,(h^2+k^2)^4} \tag{E4}$$

$$= \frac{2^7}{3^8\pi}\int_0^{\infty}\frac{\mathrm{d}k}{(1+k)(1+b^2k^2)^4} \qquad (b \equiv h^{-1}\omega_{21} = \tfrac{1}{4}\alpha). \tag{E5}$$

In (E5), (F2) can be used to calculate the integral J_4^+ exactly; but approximation (F8) is valid here, since $b \ll 1$:

$$J_4^+ \simeq -\log\frac{\alpha}{4} - \frac{11}{12}. \tag{E6}$$

This gives

$$\delta E_{1s2p}/(\alpha^5 mc^2) = 3.35 \times 10^{-2}. \tag{E7}$$

(b) $n = 2p, \nu = 3s$. Using (B8), (A4), (A5) and $\omega_{23} = -5\alpha/(72a)$ in (9) we obtain

$$\frac{\delta E_{2p3s}}{\alpha^5 mc^2} = \frac{5}{3^{12} 2\pi a^8}\int_0^\infty \frac{\mathrm{d}k}{(5\alpha/72a)+k}\left[-\frac{27}{(h^2+k^2)^2} + \frac{4}{a^2}\frac{9k^2+5h^2}{(h^2+k^2)^4}\right]^2 \tag{E8}$$

($h \equiv 5/6a$). (E8) can be split into five integrals J_i^+, $i = 4$ to 8, with $b \equiv h^{-1}\omega_{32} = \alpha/12$. Approximation (F8) leads to

$$\frac{\delta E_{2p3s}}{\alpha^5 mc^2} \simeq -\frac{2^7}{5^9\pi}\left(\log\frac{\alpha}{12} + \frac{583}{25\times 28}\right) \tag{E9}$$

$$= 1.37 \times 10^{-4}. \tag{E10}$$

(c) $n = 1s, \nu = 3p$. Using (B10), (A4), (A5) and $\omega_{13} = -4\alpha/(9a)$ in (9) we obtain

$$\frac{\delta E_{1s3p}}{\alpha^5 mc^2} = \frac{2^{12}}{3^{11}\pi a^8}\int_0^\infty \frac{\mathrm{d}k}{(4\alpha/9a)+k}\left[\frac{3}{(h^2+k^2)^2} - \frac{2h}{a(h^2+k^2)^3}\right]^2 \tag{E11}$$

($h \equiv 4/3a$). (E11) can be split into three integrals J_i^+, $i = 4, 5, 6$, with $b \equiv h^{-1}\omega_{31} = \alpha/3$. Approximation (F8) leads to

$$\frac{\delta E_{1s3p}}{\alpha^5 mc^2} \simeq -\frac{1}{3\pi 2^6}\left(\log\frac{\alpha}{3} + \frac{77}{120}\right) \tag{E12}$$

$$= 0.89 \times 10^{-2}. \tag{E13}$$

(d) $n = 2s, \nu = 3p$. Using (B12), (A4), (A5) and $\omega_{23} = -5\alpha/(72a)$ in (9) we obtain

$$\frac{\delta E_{2s3p}}{\alpha^5 mc^2} = \frac{2^2 5}{3^{11}\pi a^8}\int_0^\infty \frac{\mathrm{d}k}{(5\alpha/72a)+k}\left[-\frac{6}{(h^2+k^2)^2} + \frac{28}{3a^2(h^2+k^2)^3} - \frac{25}{6a^4(h^2+k^2)^4}\right]^2 \tag{E14}$$

($h \equiv 5/6a$). (E14) can be split into five integrals J_i^+, $i = 4$ to 8, with $b \equiv h^{-1}\omega_{32} = \alpha/12$. Approximation (F8) leads to

$$\frac{\delta E_{2s3p}}{\alpha^5 mc^2} \simeq -\frac{2^{12}}{3\pi 5^9}\left(\log\frac{\alpha}{12} + \frac{2729}{12\times 7\times 25}\right) \tag{E15}$$

$$= 1.36 \times 10^{-3}. \tag{E16}$$

(e) $n = 2p_z, \nu = 3p_z$. Using (B14), (A4), (A6) and $\omega_{23} = -5\alpha/(72a)$ in (9) we obtain

$$\frac{\delta E_{2p3p}}{\alpha^5 mc^2} = \frac{2^2 5^2}{3^{13}\pi a^{14}} \int_0^\infty \mathrm{d}k \, \frac{k^2}{((5\alpha/72a)+k)\,(h^2+k^2)^8} \tag{E17}$$

($h \equiv 5/6a$). (E17) can be converted into integrals J_7^+ and J_8^+, $b \equiv h^{-1}\omega_{32} = \alpha/12$. Approximation (F8) gives

$$\frac{\delta E_{2p3p}}{\alpha^5 mc^2} \simeq \frac{2^{15}3}{5^{12}7\pi} = 1.8 \times 10^{-5}. \tag{E18}$$

(f) $n = 2p_z, \nu = 3p_x$. Using (A4), equation (12) is written in this case

$$\int_k = -\pi \int_0^\infty \frac{\mathrm{d}k}{\omega_{32}+k} \int_0^\pi \mathrm{d}\beta \, \sin\beta \Big[\boldsymbol{T}^{\perp}_{3p_x 2p_z}(k, \pi-\beta) \cdot \boldsymbol{T}^{\perp}_{3p_x 2p_z}(k,\beta) + \boldsymbol{T}^{\perp}_{3p_y 2p_z}(k, \pi-\beta) \cdot \boldsymbol{T}^{\perp}_{3p_y 2p_z}(k,\beta) \Big] \tag{E19}$$

where the orbitals $2p_z, 3p_x$ and $3p_y$ have their axes respectively on $\boldsymbol{e}_3, \boldsymbol{i}$ and $\boldsymbol{j}'$. After (B2), the first term in the brackets of (E19) is zero. When the remaining term of (E19) is calculated with the help of (B16), and inserted in (1), we obtain

$$\frac{\delta E}{\alpha^5 mc^2} = \frac{2\times 5}{3^8 \pi a^{10}} \int_0^\infty \frac{\mathrm{d}k}{\omega_{32}+k} \int_0^\pi \mathrm{d}\beta \, \sin\beta \{\cos^2(2\beta)[1]^2 + 4\cos(2\beta)\sin^2\beta[1][2] + 4\sin^4\beta[2]^2\} \tag{E20}$$

with the notation

$$[1] \equiv \frac{k}{(h^2+k^2)^3} - \frac{5k}{6a^2(h^2+k^2)^4} \tag{E21}$$

$$[2] \equiv \frac{k}{(h^2+k^2)^3} - \frac{25k}{36a^2(h^2+k^2)^4}. \tag{E22}$$

(E20) can be split into four integrals $J_i^+, i = 4$ to 8, with $b \equiv h^{-1}\omega_{32} = 6a/5$. Approximation (F8) leads to

$$\delta E_{2p_z 3p_x}/(\alpha 5 mc^2) \simeq \frac{2^{11}11^2}{5^{12}7\pi} = 4.61 \times 10^{-5}.$$

Appendix F

In this appendix we evaluate integrals of the form

$$J_n^\pm \equiv \int_0^\infty \frac{\mathrm{d}x}{(1\pm x)(1+b^2x^2)^n} \tag{F1}$$

(n integer, b real) and relation between J_n^+ and J_n^-.

In the case of J_n^-, the integral is defined in principal value. The same method as that applied to J_n^+ in .[12] may be applied to J_n^-, leading to the recursion relationship

$$J_n^\pm(1+b^2) = J_{n-1}^\pm + b^2 I_n \mp \frac{1}{2(n-1)} \qquad (n \geqslant 2) \tag{F2}$$

with I_n defined as

$$I_n \equiv \int_0^\infty \frac{\mathrm{d}x}{(1+b^2x^2)^n} = \frac{\pi(2n-3)!}{b(n-1)!(n-2)!2^{2n-2}} \tag{F3}$$

and

$$J_1^\pm = \frac{1}{1+b^2}\left(b\frac{\pi}{2} \mp \log b\right). \tag{F4}$$

The sum

$$J_n \equiv J_n^+ + J_n^- \tag{F5}$$

satisfies the recursion relation

$$J_n(1+b^2) = J_{n-1} + 2b^2 I_n \tag{F6}$$

which leads to

$$J_n = b\pi(1+b^2)^{-n}\left[1 + 2\sum_{p=1}^{n-1}(1+b^2)^p \frac{(2p-1)!}{p!(p-1)!2^{2p}}\right]. \tag{F7}$$

For $b \ll 1$, we have

$$J_n^\pm \simeq \mp\left(\log b + \frac{1}{2}\sum_{j=1}^{n-1}\frac{1}{j}\right) \tag{F8}$$

and

$$J_n \simeq b\pi\left[1 + 2\sum_{p=1}^{n-1}\frac{(2p-1)!}{p!(p-1)!2^{2p}}\right] \tag{F9}$$

is small. In the first approximation

$$J_n^+ \simeq -J_n^-. \tag{F10}$$

Property (F10) is better understood when J_n^- is written as

$$J_n^- = \int_{-\infty}^0 \frac{\mathrm{d}x}{(1+x)(1+b^2x^2)^n}. \tag{F11}$$

Then we see that

$$J_n^+ + J_n^- = \int_{-\infty}^\infty \frac{\mathrm{d}x}{(1+x)(1+b^2x^2)^n} \tag{F12}$$

is slightly different from zero because the corrective factor $(1+b^2x^2)^{-n}$ to the hyperbola $(1+x)^{-1}$ is not symmetrical with respect to the asymptote $x = -1$

$$\left(\int_{-\infty}^\infty \frac{\mathrm{d}x}{(1+x)(1+b^2(x+1)^2)^n} \qquad \text{would be zero}\right). \tag{F13}$$

Appendix G. Calculations of form factors $T^{\perp}_{\nu\mathrm{p},1\mathrm{s}}$ for any value of ν

For levels $1\mathrm{s} \equiv (nlm) = (1,0,0)$ and $\nu\mathrm{p}_z \equiv (\nu\lambda\mu) = (\nu,1,0)(\nu \geqslant 2$; axis $\boldsymbol{e}_3$), (A19) is written as

$$T^{\perp}(\boldsymbol{k}) = -j\frac{\sqrt{3}}{\pi}\frac{2}{\nu^3}\sqrt{\frac{(\nu-2)!}{(\nu+1)!^3}}\int_0^{\infty} \mathrm{d}r\, r^3 \mathrm{e}^{-r(1/\nu+1)} L^3_{\nu-2}\left(\frac{2r}{\nu}\right) L^1_0(2r) {}^1\!\!\int_{\theta} \tag{G1}$$

with

$${}^1\!\!\int_{\theta} = \pi \sin\beta\ \Theta_{30}(kr) \qquad (\beta \equiv \mathrm{angle}(\boldsymbol{e}_3, \boldsymbol{k})). \tag{A21}$$

Replacing Θ_{30} by its value (C6) yields

$$T^{\perp} = j\frac{8\sqrt{3}\sin\beta}{\nu^3(\nu+1)!\sqrt{(\nu+1)\nu(\nu-1)}}\frac{1}{k^2}\int_0^{\infty} \mathrm{d}r\, r\mathrm{e}^{-hr} L^3_{\nu-2}\left(\frac{2r}{\nu}\right) \times \left[\cos(kr) - \frac{1}{kr}\sin(kr)\right] \tag{G2}$$

where $h \equiv 1 + 1/\nu$ and the Laguerre polynomial is

$$L^3_{\nu-2}\left(\frac{2r}{\nu}\right) = \sum_{q=0}^{\nu-2} a_q(\nu) r^q \tag{G3}$$

$$a_q(\nu) = (-1)^q \frac{(\nu+1)!^2}{(\nu-2-q)!(3+q)!q!}\left(\frac{2}{\nu}\right)^q. \tag{G4}$$

In terms of the C_n and S_n integrals (appendix D), the integral in (G2) is written

$$\int_0^{\infty} = C + S \tag{G5}$$

with

$$C \equiv \sum_{q=0}^{\nu-2} a_q(\nu) C_{q+1}(h,k) \tag{G6}$$

$$S \equiv -\frac{1}{k}\sum_{q=0}^{\nu-2} a_q(\nu) s_q(h,k). \tag{G7}$$

The C_{q+1} and S_q integrals are equal to [15]

$$C_{q+1}(h,k) = \frac{(q+1)!}{(h^2+k^2)^{(q+2)/2}}\cos((q+2)t) \tag{G8}$$

$$S_q(h,k) = \frac{q!}{(h^2+k^2)^{(q+1)/2}}\sin((q+1)t) \tag{G9}$$

using the notation

$$t \equiv \tan^{-1}\frac{k}{h} \qquad 0 \leqslant t < \frac{\pi}{2}. \tag{G10}$$

Considering the cosine in (G8) as the real part of $\exp(\mathrm{i}(q+2)t)$, we obtain

$$C = \mathrm{Re}\left\{-(\nu+1)!(\nu+1)\nu(\nu-1)\left(\frac{\nu}{2}\right)^3\sqrt{h^2+k^2}\,\mathrm{e}^{-\mathrm{i}t}\sum_{q=0}^{\nu-2}\binom{\nu-2}{q}\frac{Y^{q+3}}{(q+2)(q+3)}\right\} \tag{G11}$$

where Y is defined as

$$Y \equiv \frac{-2\mathrm{e}^{\mathrm{i}t}}{\nu\sqrt{h^2+k^2}} = -\frac{2}{\nu}\frac{h+\mathrm{i}k}{h^2+k^2}. \tag{G12}$$

The second derivative Σ'' with respect to Y of the sum Σ in (G11) is

$$\Sigma'' = Y\sum_{q=0}^{\nu-2}\binom{\nu-2}{q}Y^{q+1} = Y(1+Y)^{\nu-2}. \tag{G13}$$

Hence

$$\Sigma = \frac{(1+Y)^\nu}{\nu(\nu+1)}\left(Y - \frac{2}{\nu-1}\right) + DY + E. \tag{G14}$$

The D and E constants are determined by the conditions $\Sigma = 0$ and $\Sigma' = 0$ for $Y = 0$. We finally obtain

$$C = (\nu+1)!\frac{\nu^2}{4}\mathrm{Re}\left\{(1+Y)^\nu\left(\nu-1-\frac{2}{Y}\right)+\nu+1+\frac{2}{Y}\right\}. \tag{G15}$$

Let $\rho(\nu,k)$ and $\theta(\nu,k)$ be the magnitude and argument of $1+Y$;

$$\rho\mathrm{e}^{\mathrm{i}\theta} \equiv 1+Y. \tag{G16}$$

We have

$$C = (\nu+1)!\frac{\nu^3}{4}\rho^\nu[2\cos(\nu\theta)+k\sin(\nu\theta)]. \tag{G17}$$

To calculate S, we consider the sine in (G9) as the imaginary part of $\exp(\mathrm{i}(q+1)t)$. This gives

$$S = \frac{1}{k}(\nu+1)!\frac{\nu^3}{8}(h^2+k^2)\mathrm{Im}\left\{\mathrm{e}^{-\mathrm{i}2t}\sum_{q=3}^{\nu+1}\binom{\nu+1}{q}Y^q\right\} \tag{G18}$$

where Y is still defined as in (G12). The sum Σ in (G18) is equal to

$$\Sigma = (1+Y)^{\nu+1} - 1 - (\nu+1)Y - \frac{(\nu+1)\nu}{2}Y^2 \tag{G19}$$

and therefore

$$S = \frac{1}{k}(\nu+1)!\frac{\nu}{2}\mathrm{Im}\{Y^{-2}(1+Y)^{\nu+1} - Y^{-2} - (\nu+1)Y^{-1}\}. \tag{G20}$$

Using

$$\mathrm{Re}\,[Y^{-2}(1+Y)] = \frac{\nu^2}{4}\left(-\frac{2h}{\nu} + h^2 - k^2\right) \tag{G21}$$

and

$$\mathrm{Im}\,[Y^{-2}(1+Y)] = -\frac{\nu^2}{2}k \tag{G22}$$

and introducing ρ, θ as defined by (G16), we obtain

$$S = \frac{1}{k}(\nu+1)!\frac{\nu^2}{4}\rho^\nu\left[\left(-h + \frac{\nu}{2}(h^2-k^2)\right)\sin(\nu\theta) - k\nu\cos(\nu\theta)\right]. \tag{G23}$$

Substitution of (G17) and (G23) into (G5) gives for the integral in (G2)

$$\int_0^\infty = (\nu+1)!\frac{\nu^2}{4}\rho^\nu\left[\nu\cos(\nu\theta) + \sin(\nu\theta)\left(-\frac{h}{k} + \frac{\nu}{2}\frac{h^2+k^2}{k}\right)\right]. \tag{G24}$$

Using (G24), and introducing the Bohr radius a again as indicated in appendix A, we obtain for $\boldsymbol{T}^\perp$:

$$\boldsymbol{T}^\perp_{\nu\mathrm{p1s}}(\boldsymbol{k}) = \boldsymbol{j}\frac{2\sqrt{3}\sin\beta}{\sqrt{(\nu+1)\nu(\nu-1)a^3k^2}}\rho^\nu\left[\cos(\nu\theta) + \sin(\nu\theta)\left(-\frac{h}{\nu k} + \frac{a(h^2+k^2)}{2k}\right)\right] \tag{G25}$$

with

$$h \equiv \frac{1}{a}\left(1 + \frac{1}{\nu}\right) \tag{G26}$$

$$\rho \equiv \sqrt{1 - \frac{4}{a^2\nu(h^2+k^2)}} \tag{G27}$$

$$\theta \equiv \tan^{-1}\frac{k}{h - a\nu(h^2+k^2)/2} \qquad -\frac{\pi}{2} < \theta \leqslant 0. \tag{G28}$$

Notice that the coefficient of $\sin(\nu\theta)$ in the bracket of (G25) is also equal to $-\nu^{-1}\cot\theta$.

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