

Relativistic Corrections of Closed-shell Atomic Systems

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Abstract

Analytical expressions for the relativistic energy associated with closed-shell atomic systems have been given by Hartmann and Clementi (1964). We derive a new set of analytical expressions and conclude that those of Hartmann and Clementi are in error.

In the theory of atomic structure we are concerned with electrons interacting with each other as well as with an external electromagnetic field. The Dirac theory is not sufficient. The most commonly used approximation for describing the relativistic interaction between electrons in an approximate way is the Breit interaction. The relativistic corrections to the nonrelativistic energy may be determined to order $(\alpha Z)^2$ (where α is the fine structure constant) in terms of the Breit operator by first-order perturbation theory (Bethe and Salpeter 1972). That is, these corrections are given as the expectation value of the Breit operator with respect to the zero-order wave-function ϕ_0 , which satisfies

$$H_0 \phi_0 = \left(\sum_i h_i + \sum_{i < j} r_{ij}^{-1} \right) \phi_0 = E_0 \phi_0, \quad (1)$$

where h_i is the one-electron Dirac operator.

Hartmann and Clementi (1964) have derived simple analytic expressions for the relativistic corrections of closed-shell atomic systems. Unfortunately their expressions are in error.

For a closed-shell N -electron atomic system the relativistic correction can be written (in a.u.) as

$$H_{\text{rel}} = H_m + H_{d1} + H_{d2} + H_{\text{ssc}} + H_{\text{oo}}, \quad (2)$$

where

$$H_m = -\frac{1}{8}\alpha^2 \sum_{i=1}^N \nabla_i^4 \quad (3)$$

is the relativistic mass correction, giving the variation of mass with velocity;

$$H_{d1} = -\frac{1}{8}\alpha^2 Z \sum_{i=1}^N \nabla_i^2 (1/r_i) \quad (4)$$

is the one-body Darwin term, giving the relativistic correction to the potential energy;

$$H_{d2} = \frac{1}{4}\alpha^2 \sum_{i < j} \nabla_i^2 (1/r_{ij}) \quad (5)$$

is the two-body Darwin term, giving the relativistic correction to the potential energy;

$$H_{ssc} = -\frac{8}{3}\pi\alpha^2 \sum_{i < j} (s_i \cdot s_j) \delta(r_i - r_j) \quad (6)$$

is the electron spin-spin contact term; and

$$H_{oo} = -\frac{1}{2}\alpha^2 \sum_{i < j} \left(\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}} + \frac{\mathbf{r}_{ij}(\mathbf{r}_{ij} \cdot \mathbf{p}_i) \cdot \mathbf{p}_j}{r_{ij}^3} \right) \quad (7)$$

is the orbit-orbit interaction.

Hartmann and Clementi (1964) omitted the contribution from the orbit-orbit operator. The contribution from the matrix elements of the orbit-orbit operator for closed-shell atomic systems has been derived by Walker (1971). In the present paper we will only derive energy expressions for the terms included by Hartmann and Clementi. For the contributions from the orbit-orbit interaction we refer the reader to the paper by Walker.

Provided that the wavefunction is antisymmetric with respect to interchange of the i th and j th electrons, the operator $-\frac{4}{3}(s_i \cdot s_j)$ has the same matrix element as the unit operator with respect to spin. Thus, since our wavefunctions are antisymmetric, we may write the spin-spin contact term as

$$H_{ssc} = 2\pi\alpha^2 \sum_{i < j} \delta(r_i - r_j). \quad (8)$$

From the potential equation

$$\nabla^2(1/r_{ij}) = -4\pi \delta(r_i - r_j), \quad (9)$$

the two-body Darwin term reduces to

$$H_{d2} = -\pi\alpha^2 \sum_{i < j} \delta(r_i - r_j). \quad (10)$$

Hence we can write the spin-spin contact and two-body Darwin terms as

$$H_{sscd2} = H_{ssc} + H_{d2} = \pi\alpha^2 \sum_{i < j} \delta(r_i - r_j). \quad (11)$$

Expressing $\delta(r_i - r_j)$ in tensor form as

$$\delta(r_i - r_j) = \frac{1}{4\pi} \frac{\delta(r_i - r_j)}{r_i r_j} \sum_k (2k+1) \{C^{[k]}(i) \cdot C^{[k]}(j)\}, \quad (12)$$

equation (11) reduces to

$$H_{sscd2} = \frac{1}{4}\alpha^2 \sum_{i < j} \frac{\delta(r_i - r_j)}{r_i r_j} \sum_k (2k+1) \{C^{[k]}(i) \cdot C^{[k]}(j)\}, \quad (13)$$

and the components of the spherical tensor $C^{[k]}$ satisfy the equation

$$C_\mu^{[k]} = \{4\pi/(2k+1)\}^{\frac{1}{2}} Y_k^\mu. \quad (14)$$

The configurational wavefunctions $\{\Phi_j\}$ are built from a set of one-electron functions (spin orbitals)

$$u_{nlm_l}(r, m_s) = r^{-1} P_{nl}(r) Y_l^{m_l}(\theta, \phi) \chi(m_s), \quad (15)$$

where the radial functions P_{nl} ; $n = l+1, \dots$, form an orthonormal set.

The relativistic mass correction energy is given by

$$E_m = \langle \Phi | -\frac{1}{8}\alpha^2 \sum_{i=1}^N \nabla_i^4 | \Phi \rangle \quad (16)$$

$$= -\frac{1}{8}\alpha^2 \sum_{\rho\rho'} x(\rho\rho') \langle P_{n\rho l\rho}(r) | \nabla^4 | P_{n\rho' l\rho'}(r) \rangle, \quad (17)$$

where ρ and ρ' are the 'interacting' subshells. For closed-shell systems $\rho = \rho'$ and $x(\rho\rho') = N_\rho$ is the number of electrons in the subshell ρ , and

$$\langle P_{n\rho l\rho}(r) | \nabla^4 | P_{n\rho' l\rho'}(r) \rangle = \langle \nabla^2 P_{n\rho l\rho}(r) | \nabla^2 P_{n\rho l\rho}(r) \rangle. \quad (18)$$

Thus, we get

$$E_m = -\frac{1}{4}\alpha^2 \sum_{n\rho l\rho} (2l_\rho + 1) \{ I_1(n_\rho l_\rho) - 2l_\rho(l_\rho + 1) I_3(n_\rho l_\rho) + l_\rho^2(l_\rho + 1)^2 I_4(n_\rho l_\rho) \}, \quad (19)$$

where

$$I_1(n_\rho l_\rho) = \int_0^\infty \left(\frac{d^2}{dr^2} \{ P_{n\rho l\rho}(r) \} \right)^2 dr, \quad (20)$$

$$I_3(n_\rho l_\rho) = \int_0^\infty (1/r^2) \frac{d^2}{dr^2} \{ P_{n\rho l\rho}(r) \} P_{n\rho l\rho}(r) dr, \quad (21)$$

$$I_4(n_\rho l_\rho) = \int_0^\infty (1/r^4) \{ P_{n\rho l\rho}(r) \}^2 dr. \quad (22)$$

For the one-body Darwin energy we have

$$E_{d1} = \langle \Phi | -\frac{1}{8}\alpha^2 Z \sum_{i=1}^N \nabla_i^2 (1/r_i) | \Phi \rangle \quad (23)$$

$$= \frac{1}{8}\alpha^2 Z \langle \Phi | \sum_{i=1}^N \delta(r_i)/r_i^2 | \Phi \rangle \quad (24)$$

$$= \frac{1}{8}\alpha^2 Z \sum_{\rho\rho'} x(\rho\rho') \langle P_{n\rho l\rho}(r) | \delta(r)/r^2 | P_{n\rho' l\rho'}(r) \rangle \quad (25)$$

$$= \frac{1}{4}\alpha^2 \sum_{n\rho 0} I_5(n_\rho 0), \quad (26)$$

where

$$I_5(n_\rho 0) = Z [(1/r^2) \{ P_{n\rho 0}(r) \}^2]_{r=0}, \quad (27)$$

Further, we have

$$E_{sscd2} = \langle \Phi | \frac{1}{4}\alpha^2 \sum_{i < j} \frac{\delta(r_i - r_j)}{r_i r_j} \sum_k (2k+1) \{ C^{[k]}(i) \cdot C^{[k]}(j) \} | \Phi \rangle \quad (28)$$

$$= \frac{1}{4}\alpha^2 \sum_{\rho\sigma\rho'\sigma',k} (2k+1) y(\rho\sigma\rho'\sigma'k) \\ \times \langle P_{n\rho l\rho}(r) P_{n\sigma l\sigma}(r) | \delta(r_i - r_j)/r_i r_j | P_{n\rho' l\rho'}(r) P_{n\sigma' l\sigma'}(r) \rangle, \quad (29)$$

where $\rho, \sigma, \rho', \sigma'$ are the 'interacting' subshells. For closed-shell systems $\rho = \rho'$ and $\sigma = \sigma'$, whence (29) simplifies to

$$E_{\text{sscd}2} = \frac{1}{4}\alpha^2 \left\{ \sum_{n\rho l\rho} \left((2l_\rho + 1)(4l_\rho + 1) - \sum_{k>0} (2k+1) (\langle l_\rho \| C^{[k]} \| l_\rho \rangle)^2 \right) I_2(n_\rho l_\rho) \right. \\ \left. + \sum_{n\rho l\rho < n\sigma l\sigma} \left(4(2l_\rho + 1)(2l_\sigma + 1) - 2 \sum_k (2k+1) (\langle l_\rho \| C^{[k]} \| l_\sigma \rangle)^2 \right) \right. \\ \left. \times I(n_\rho l_\rho, n_\sigma l_\sigma) \right\} \quad (30)$$

$$= \frac{1}{4}\alpha^2 \left[\sum_{n\rho l\rho} (2l_\rho + 1)(4l_\rho + 1) \left(1 - \frac{2l_\rho + 1}{4l_\rho + 1} \sum_{k>0} (2k+1) \begin{pmatrix} l_\rho & k & l_\rho \\ 0 & 0 & 0 \end{pmatrix}^2 \right) I_2(n_\rho l_\rho) \right. \\ \left. + \sum_{n\rho l\rho < n\sigma l\sigma} 4(2l_\rho + 1)(2l_\sigma + 1) \left(1 - \frac{1}{2} \sum_k (2k+1) \begin{pmatrix} l_\rho & k & l_\sigma \\ 0 & 0 & 0 \end{pmatrix}^2 \right) I(n_\rho l_\rho, n_\sigma l_\sigma) \right] \quad (31)$$

$$= \frac{1}{4}\alpha^2 \left(\sum_{n\rho l\rho} (2l_\rho + 1)^2 I_2(n_\rho l_\rho) + \sum_{n\rho l\rho < n\sigma l\sigma} 2(2l_\rho + 1)(2l_\sigma + 1) I(n_\rho l_\rho, n_\sigma l_\sigma) \right), \quad (32)$$

where

$$I_2(n_\rho l_\rho) = \int_0^\infty (1/r^2) \{P_{n\rho l\rho}(r)\}^4 dr, \quad (33)$$

$$I(n_\rho l_\rho, n_\sigma l_\sigma) = \int_0^\infty (1/r^2) \{P_{n\rho l\rho}(r) P_{n\sigma l\sigma}(r)\}^2 dr; \quad (34)$$

$$I(n_\rho l_\rho, n_\sigma l_\sigma) = I(n_\sigma l_\sigma, n_\rho l_\rho). \quad (35)$$

Comparing equations (26) and (32) with (10b) of Hartmann and Clementi (1964) we see that the factor $2l+1$ in (10b) should be $(2l+1)^2$. The contribution from the 'interacting' subshells ρ and σ is also missing. This is due to an error in their energy expressions E_4 and E_5 . The second and third terms of E_4 are the contributions from the two-body Darwin term. From our equations (10) and (11) the contribution from the two-body Darwin term (except for a factor of -1) is the same as the contribution from $H_{\text{sscd}2}$. From (30) we see that Hartmann and Clementi have omitted the contribution from the interacting subshells ρ and σ . Their energy expression E_5 is for the contribution from the spin-spin contact term. From equations (8) and (11) the contribution from the spin-spin contact term is twice the contribution from $H_{\text{sscd}2}$ and from (30) we see that they have omitted the contribution from electrons in the same subshell ρ . Also, the expression given by them should be multiplied by -1 .

The total relativistic energy E_{rel} is therefore given by

$$E_{\text{rel}} = E_m + E_{d1} + E_{\text{sscd}2} \quad (36) \\ = -\frac{1}{4}\alpha^2 \left(\sum_{n\rho l\rho} (2l_\rho + 1) I_1(n_\rho l_\rho) - (2l_\rho + 1)^2 I_2(n_\rho l_\rho) \right. \\ \left. - (l_\rho + 1) 2l_\rho (2l_\rho + 1) I_3(n_\rho l_\rho) \right)$$

$$+ l_\rho^2(l_\rho + 1)^2(2l_\rho + 1)I_4(n_\rho l_\rho) - I_5(n_\rho 0) \\ - \sum_{n_\rho l_\rho < n_\sigma l_\sigma} 2(2l_\rho + 1)(2l_\sigma + 1)I(n_\rho l_\rho, n_\sigma l_\sigma) \quad (37)$$

$$= -\frac{1}{4}\alpha^2 \left(\sum_{n_\rho l_\rho, i} a_{n_\rho l_\rho i} I_i(n_\rho l_\rho) \right. \\ \left. - \sum_{n_\rho l_\rho < n_\sigma l_\sigma} 2(2l_\rho + 1)(2l_\sigma + 1)I(n_\rho l_\rho, n_\sigma l_\sigma) \right), \quad (38)$$

where $i = 1, 2, 3, 4, 5$. The coefficients that are needed for the computation of relativistic energies of closed-shell systems are given in Tables 1 and 2.

Table 1. Coefficients $a_{n_\rho l_\rho i}$ for closed-shell configurations

$n_\rho l_\rho = n_\sigma l_\sigma$	$a_{n_\rho l_\rho 1}$	$a_{n_\rho l_\rho 2}$	$a_{n_\rho l_\rho 3}$	$a_{n_\rho l_\rho 4}$	$a_{n_\rho l_\rho 5}$
$n_\rho s$	1	-1	0	0	-1
$n_\rho p$	3	-9	-12	12	0
$n_\rho d$	5	-25	-60	180	0
$n_\rho f$	7	-49	-168	1008	0

Table 2. Coefficients for $n_\rho l_\rho \neq n_\sigma l_\sigma$

$n_\rho s n_\sigma s$	2	$n_\rho p n_\sigma p$	18	$n_\rho d n_\sigma d$	50
$n_\rho s n_\sigma p$	6	$n_\rho p n_\sigma d$	30	$n_\rho d n_\sigma f$	70
$n_\rho s n_\sigma d$	10	$n_\rho p n_\sigma f$	42		
$n_\rho s n_\sigma f$	14				

Furthermore, the coefficients given by Hartmann and Clementi (in their Table 1) are in error. The coefficients given for d_{n11} are those for d_{n14} and vice versa. Also the coefficients given for d_{n12} , d_{n13} and d_{n15} should be negative.

The Hartmann and Clementi paper is a generalization of the theory originally presented by Fröman (1958), who derived analytical expressions for the helium- and neon-isoelectronic sequences. There are two errors in his equation (17): (i) the factor $\frac{21}{5}$ should read -9 and (ii) the contributions from the interacting subshells ρ and σ are omitted.

The relativistic corrections (A11) given by Cohen and McEachran (1980) are also in error. They assumed that the energy shift given by Hartmann and Clementi was correct.

References

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