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HYPERFINE INTERACTIONS BETWEEN ELECTRONS

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Abstract

The relativistic Breit Hamiltonian between electrons is transformed into an effective vector potential $\mathbf{A}_i$ for the i.th electron, $\mathbf{A}_i$ having the structure of a recoil–corrected hyperfine operator. Apart from a small three–body operator, the Dirac–Breit equation is now easier applied to relativistic magnetic properties of complex systems.

Relativistic n–electron systems of atoms or molecules are quite precisely described by the Dirac–Breit equation [1]. In addition to the ordinary Dirac–Coulomb Hamiltonian, the equation contains the Breit Hamiltonian [2]

$$H_B = \sum_{i<j} B_{ij}\,, \qquad B_{ij} = -e^2(\boldsymbol{\alpha}_i\boldsymbol{\alpha}_j + \alpha_{ir}\alpha_{jr})/2r_{ij}\,, \tag{1}$$

where the $\boldsymbol{\alpha}$ are Dirac matrices and α_{ir} and α_{jr} are the components of $\boldsymbol{\alpha}_i$ and $\boldsymbol{\alpha}_j$ along the direction $\hat{\mathbf{r}}$ of $\mathbf{r}_i - \mathbf{r}_j$. H_B contributes to the electronic fine structure. The term hyperfine interaction is normally reserved for the interaction with the nuclear spin [3].

Breit operators are somewhat inconvenient. Firstly, H_B is the only operator in the Dirac–Breit equation which exchanges large and small components of two electrons simultaneously. Secondly, the use of H_B beyond first–order perturbation theory requires complicated *improved versions* of B_{ij} [4]. This is so because B_{ij}^2 is too large.

In this letter we present a transformation which removes both inconveniences. One of the new operators produced by the transformation is complicated but should be negligible. Without it, the Dirac–Breit equation for n electrons of total energy E with a total potential $V = \sum V(\mathbf{r}_i) + \sum_{i<j} e^2/r_{ij}$ becomes

$$\left[E - V - mc^2\sum\beta_i - \sum\boldsymbol{\alpha}_i(c\mathbf{p}_i + e\mathbf{A}_{0i} + e\mathbf{A}_{\mathrm{hf},i})\right]\Psi = 0\,. \tag{2}$$

Here $\mathbf{A}_{0i}$ is the vector potential produced by spinless electrons,

$$\mathbf{A}_{0i} = -\frac{e}{4mc}\sum_{j\neq i} r_{ij}^{-1}(\mathbf{p}_j + \hat{\mathbf{r}}_{ij}p_{jr}) \tag{3}$$

and $\mathbf{A}_{\mathrm{hf},i}$ is the vector potential of the electron spins

$$\mathbf{A}_{\mathrm{hf},i} = -\frac{e}{4mc}\nabla_i \times \sum_{j\neq i}\boldsymbol{\sigma}_j/r_{ij}\,. \tag{4}$$

This is nothing but the ordinary hyperfine interaction with spinor particles j of g–factors $g_j = 2$ and masses m_j, for the special case $m_i = m_j = m$. If one is only interested in spin–polarized systems, $\mathbf{A}_{0i}$ may also be neglected.

The operator $\mathbf{p}_i = -i\hbar\nabla_i$ is the canonical momentum. The momentum which enters the kinetic energy is $\boldsymbol{\pi}_i = \mathbf{p}_i + e\mathbf{A}_i/c$. One may therefore say that the Breit operator has become part of the kinetic energy. This form could be useful e.g. for relativistic density functional theories, in which the $\mathbf{A}$ appearing in the Kohn–Sham equations represents more than an external magnetic field [5].

For the derivation of (2) from the Dirac–Breit equation it is convenient to decompose $\boldsymbol{\alpha} = \gamma_5 \boldsymbol{\sigma}$, where the $\boldsymbol{\sigma}$ are Pauli matrices; γ_5 exchanges large and small components. The B_{ij} of (1) becomes

$$B_{ij} = -\gamma_{5i}\gamma_{5j}\, b_{ij}\ , \qquad b_{ij} = (\boldsymbol{\sigma}_i \boldsymbol{\sigma}_j + \sigma_{ir}\sigma_{jr})e^2/2r_{ij}\,. \tag{5}$$

As $\gamma_5^2 = 1$, one finds $B_{ij}^2 = b_{ij}^2$, which is unacceptably large [3]. The improved versions of B_{ij} [4] give much smaller B_{ij}^2. In the following we simply keep B_{ij} (5) but put $B_{ij}^2 = 0$ by hand [6]. We also abbreviate

$$E - V = c\pi^0, \qquad \sum \boldsymbol{\alpha}_i \mathbf{p}_i = P \tag{6}$$

which gives the original Dirac–Breit equation the compact form

$$(\pi^0 - mc\sum \beta_i - P - H_B/c)\Psi_{DB} = 0\,. \tag{7}$$

The main step in the derivation of (2) from (7) has been done in 1990 for the special case of two–electron atoms [7]. One defines an operator Z which satisfies

$$\{\pi^0 - mc\sum \beta_i\,, Z\} = H_{\mathrm{B}}/c\,, \tag{8}$$

sets $\Psi_{DB} = (1+Z)\Psi$, and multiplies (7) by $(1+Z)$. As the solution Z of (8) is proportional to B_{ij}, one neglects terms of order Z^2 and $Z\,B_{ij}$, thus obtaining

$$(\pi^0 - mc\sum \beta_i - P - \{P, Z\}\,)\Psi = 0\,. \tag{9}$$

Remembering $\{\beta, \gamma_5\} = 0$, one finds the following solution of (8):

$$Z = \sum_{i<j} \mathrm{B}_{ij}/2(c\pi^0 - mc^2 \sum_k{}'' \beta_k)\,. \tag{10}$$

The $''$ on the last sum means omission of terms with $k = i$ or j. For systems with only two electrons, the denominator of Z is $2c\pi^0$. For $n > 2$ electrons, Z is complicated, but when $\{P, Z\}$ in (9) is small, we may approximate $\beta_k = 1$ and also $\pi^0 = nmc$, such that the whole bracket is simply $2mc^2$.

As Z contains two factors γ_5 and P contains one, $\{P, Z\}$ contains a triple sum with three such factors. When the γ_5 from P is γ_{5i} or γ_{5j}, the relation $\gamma_5^2 = 1$ reduces the three factors γ_5 to one. The remaining terms will be called $\{P, Z\}_3$:

$$\{P, Z\} = -\sum_{i\neq j} \{\mathbf{p}_j \boldsymbol{\sigma}_j\,, b_{ij}\}\,\gamma_{5i}/4mc^2 + \{P, Z\}_3\,, \tag{11}$$

$$\{P, Z\}_3 = -\sum_{i\neq j\neq k} b_{ij}\,\mathbf{p}_k\,\boldsymbol{\sigma}_k\,\gamma_{5i}\,\gamma_{5j}\,\gamma_{5k}/2mc^2. \tag{12}$$

$\{P, Z\}_3$ is now a three–body operator which is small on account of its three factors γ_5 which exchange large and small components. Hopefully, it may be neglected in applications.

It remains to evaluate the anticommutators $\{\mathbf{p}_j\boldsymbol{\sigma}_j, b_{ij}\}$ in (11):

$$\{\mathbf{p}_j\boldsymbol{\sigma}_j, b_{ij}\} = e^2 r_{ij}^{-1}[\boldsymbol{\sigma}_i\mathbf{p}_j + \sigma_{ir}\, p_{jr} + (\boldsymbol{\sigma}_i \times \boldsymbol{\sigma}_j)_r\, /r_{ij}]\,. \tag{13}$$

The last operator in the square bracket produces $\mathbf{A}_{\mathrm{hf},i}$ by means of the identity $(\boldsymbol{\sigma}_i \times \boldsymbol{\sigma}_j)_r/r^2 = \boldsymbol{\sigma}_i(\nabla \times \boldsymbol{\sigma}_j/r)$. This completes our derivation of equation (2). It is worth mentioning that the combination $\boldsymbol{\alpha}_i\, e\mathbf{A}_{0i}$ is the Breit interaction of the i.th electron with spinless particles. It appears also for nuclei, spinless or not, with $2m$ replaced by $m_i + m_j$ in (3), and with $-e$ replaced by $Z_j e$. For a single nucleus $j = N$, one may use $\mathbf{p}_N = -\sum_{i'} \mathbf{p}_{i'}$ to remove the $\mathbf{p}_i$–contribution in $\mathbf{A}_{0i}$ by a small shift of the distance r_{iN}, $r_{iN} = r_i + Ze^2/2(m + m_N)c^2$ [6].

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