

Relativistic Hamiltonian for neutral atom of spin-1/2 nucleus in homogeneous magnetic field

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Abstract : A relativistic formalism to construct the Hamiltonian for a general N -electron neutral atom with a spin $\frac{1}{2}$ nucleus and placed in a homogeneous magnetic field [*J. Chem Phys* 123 064101 (2005)] is discussed here. Projected Coulomb and Breit interactions are taken to describe the inter-particle interaction through second order in fine structure constant. The center of mass motion is separated from the movement of the neutral $(N+1)$ -fermion system. Using a series of suitable unitary transformations, the Hamiltonian can be brought into a separable form. The correct atomic Hamiltonian in the non-relativistic limit is also discussed. The treatment can be extended to the case of a molecule containing atoms of only spin- $\frac{1}{2}$ nuclei.

Keywords : Relativistic Hamiltonian, projected interaction, non-relativistic limit

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1. Introduction

In most of the state of art quantum theoretical calculations on atoms and molecules, one usually considers a faceless nucleus that provides only a Coulombic potential that can be legitimately viewed as an external one. Sometimes the effects of nuclear and electron spins are treated in a perturbative manner. However, for a multi-electron atom with a different nuclear spin, one can expect that there is a different form for the Hamiltonian operator.

In our earlier work, the relativistic dynamics of one and two fermion systems placed in a homogeneous magnetic field were discussed in detail [1–3]. A generalization of this treatment has also been carried out explicitly [4]. In this work we describe the

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formulation of a relativistic Hamiltonian for a neutral N-electron atom with a spin- $\frac{1}{2}$ nucleus in simpler terms.

In Section 2 of this article, the phenomenological relativistic Hamiltonian is written for a (N+1) particle system with proper inter-particle electro-dynamical interaction [5]. In Section 3, the separation of the center of mass motion is carried out and the dynamics of each one-particle part is brought to a separable form. The non-relativistic Hamiltonian and a few general points of observation are discussed in Section 4.

2. Phenomenological Hamiltonian

The total relativistic Hamiltonian for an atom with a spin- $\frac{1}{2}$ nucleus and N electrons, and placed in a homogeneous magnetic field, can be written from a generalized version [6] of the celebrated Bethe-Salpeter equation [7]. We write

$$H = h_D(1|r_1) + \sum_{i=2}^{N+1} h_D(i|r_i) + U \quad (1)$$

where the first particle is the nucleus and rest N particles are electrons. The operator $h_D(i|r_i)$ is the Dirac Hamiltonian for the i -th particle,

$$h_D(i|r_i) = \alpha_i \cdot \pi_i + \beta_i m_i c^2 - \mu_{\text{ano}}(i) \beta_i \sigma_{iz} B. \quad (2)$$

In the above, m_i , π_i and $\mu_{\text{ano}}(i)$ are the corresponding rest mass, operator for the mechanical momentum and the anomalous magnetic moment; B is magnetic field strength, and α_i , β_i and σ_i are the respective Dirac matrices in standard representation. The last term in the above equation arises from the interaction of the anomalous magnetic moment with the external magnetic field. We adopt the symmetric gauge here for convenience, that is, $\mathbf{A}(r_i) = \frac{1}{2} \mathbf{B} \times r_i$. The mechanical momentum is written as $\pi_i = \mathbf{p}_i - \frac{q_i}{c} \mathbf{A}(r_i)$, where q_i is the charge of the i -th particle.

The interaction U is taken as projected so that it can be used safely to all orders in perturbation theory, without fear from infinite degeneracy or continuum dissolution [5],

$$U = \Lambda_+ (\mathbf{U}_B + \mathbf{U}_M) \Lambda_+. \quad (3)$$

In the above, $\Lambda_+ = \prod_{i=1}^N \lambda_{i+}$, λ_{i+} being the generalized Casimir projection operator,

$$\lambda_{i+} = \frac{1}{2} (1 + \mathbf{h}_D(i) / \mathbf{E}_i) \quad (4)$$

where \mathbf{E}_i is the diagonal form of $\mathbf{h}_D(i)$. The generalized Breit term \mathbf{U}_B is

$$\mathbf{U}_B = \sum_{1 \leq i < j \leq N+1} \frac{q_i q_j}{r_{ij}} \left[1 - \frac{\alpha_i \cdot \alpha_j}{2} - \frac{(\alpha_i \cdot r_{ij}) \cdot (\alpha_j \cdot r_{ij})}{2r_{ij}^2} \right] \quad (5)$$

where $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, contains the retardation effect through order v^2/c^2 . The magnetic interaction U_M is the Barker-Glover generalization [8] of the interaction of the *intrinsic magnetic moment* with the external electromagnetic field,

$$U_M = \sum_{1 \leq i < j \leq N+1} q_i q_j \hbar \left[-\frac{\mu_i}{2m_i c} \left(i\beta_i \alpha_i \cdot \frac{\mathbf{r}_{ij}}{r_{ij}^2} - \beta_i \sigma_i \cdot \alpha_i \times \frac{\mathbf{r}_{ij}}{r_{ij}^2} \right) + \frac{\mu_j}{2m_j c} \left(i\beta_j \alpha_j \cdot \frac{\mathbf{r}_{ij}}{r_{ij}^2} - \beta_j \sigma_j \cdot \alpha_i \times \frac{\mathbf{r}_{ij}}{r_{ij}^2} \right) \right. \\ \left. + \beta_i \beta_j \frac{q_i q_j \hbar^2 \mu_i \mu_j}{4m_i m_j c^2} \left(\sigma_i \cdot \sigma_j - \frac{3(\sigma_i \cdot \mathbf{r}_{ij})(\sigma_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} - \frac{8\pi}{3} \sigma_i \cdot \sigma_j \delta^3(\mathbf{r}_{ij}) \right) \right] \quad (6)$$

where $\mu_i = \frac{2m_i c}{q_i \hbar} \mu_{\text{ano}}(i)$ for $i = 1, \dots, N+1$. The quantity U_M is not included in the treatment in Ref. [6].

3. Simplification of dynamics

The total relativistic Hamiltonian is expressed in a new set of coordinates, $(\mathbf{R}_{CM}, \{\mathbf{r}'_i\})$. The center of mass coordinate is defined by

$$\mathbf{R}_{CM} = \sum_{i=1}^{N+1} \frac{m_i}{M_T} \mathbf{r}_i, \quad (7a)$$

and the relative coordinates are

$$\mathbf{r}'_i = \mathbf{r}_i - \mathbf{r}_1 \quad (7b)$$

where M_T is the total rest mass $M_T = \sum_{i=1}^{N+1} m_i$, and \mathbf{r}'_i are defined for $i = 2, \dots, N+1$.

This allows one to write the Dirac Hamiltonian operators as

$$h_D(1) = c \alpha_1 \cdot \left\{ \frac{m_1}{M_T} \mathbf{K} - \sum_{J=2}^{N+1} \mathbf{p}'_J - \frac{1}{c} \left(q_1 \mathbf{A}_{CM} - \sum_{J=2}^{N+1} \frac{q_J m_J - q_1 m_1}{M_T} \mathbf{A}'_J \right) \right\} \\ + \beta_1 m_1 c^2 - \mu_{\text{ano}}(1) B \beta_1 \sigma_{1z}, \quad (8)$$

and for $i = (2, N + 1)$,

$$h_D(i) = c \alpha_i \cdot \left\{ \frac{m_i}{M_T} \mathbf{K} + \mathbf{p}'_i - \frac{1}{c} \left(q_i (\mathbf{A}_{CM} + \mathbf{A}'_i) - \sum_{j(i \neq j)} \frac{q_j m_j - q_i m_i}{M_T} \mathbf{A}'_j \right) \right\} \\ + \beta_i m_i c^2 - \mu_{\text{ano}}(i) B \beta_i \sigma_{iz}.$$

The center of mass motion is also embedded in the relativistic Hamiltonian described in the previous section. The movement of the center of mass is separated from a

neutral atom following the techniques put forward by Avron *et al* [9]. It is found that the total pseudo-momentum $K = \sum_{i=1}^{N+1} k_i$ is a constant of motion for the Hamiltonian H , though the individual mechanical momentum π_i and individual pseudo-momentum $k_i = \mathbf{p}_i + \frac{q_i}{c} \mathbf{A}_i$ are not constants of motion. The components of K are found to satisfy the commutation relations $K \times K = -i \frac{Q\hbar}{c} \mathbf{B}$ where Q is the total charge written as $Q = \sum_{i=1}^{N+1} q_i$. These components are distinct only for a neutral atom. As K commutes with H , one may replace the total pseudo-momentum K by its eigenvalue K [9]. This changes the Hamiltonian $H(K)$ into the effective Hamiltonian $H(K)$ and the projectors $\lambda_{i+}(K)$ and $\Lambda_+(K)$ into the reduced projectors $\lambda_{i+}(K)$ and $\Lambda_+(K)$.

Using suitable unitary transformations one can transform the effective Hamiltonian into an exceedingly simple form. The translational motion for a neutral N-electron atom is discarded by considering the reduced Hamiltonian at zero total pseudo-momentum $H(0)$ that represents the relative movements of the particles [4],

$$H(0) = h'_D(1) + \sum_{i=2} h'_D(i) + U(0). \quad (9)$$

In the above

$$h'_D(1) = -c\alpha_1 g \sum_{i=2}^{N+1} K'_i + \beta_1 m_1 c^2 - \mu_{\text{ano}}(1) B \beta_1 \sigma_{1z}, \quad (10)$$

$$h'_D(i) = c\alpha_i g \pi'_i + \beta_i m_i c^2 - \mu_{\text{ano}}(i) B \beta_i \sigma_{iz}, \quad (\text{for } i = 2, \dots, N), \quad (11)$$

and

$$U(0) = \Lambda_+(0)(U_B + U_M)\Lambda_+(0) \quad (12)$$

with $\Lambda_+(0) = \prod_{i=1}^{N+1} \lambda_{i+}^0$ and $\lambda_{i+}^0 = \frac{1}{2} \left(1 + \frac{h'_D(i)}{E'_D(i)} \right)$ for $i = 1, \dots, N+1$.

To gain certain advantages we bring first $h'_D(1)$ and then each $h'_D(i)$ into a form that is separable for positive- and negative-energy states. In order to bring the Hamiltonian into a separable form, the odd Dirac matrices for the particles are replaced by even terms through the successive use of a set of Tsai [10] and Weaver [11] transformations, and one obtains the transformed one particle Hamiltonians as

$$h_T(1) = \beta_1 \left| \left\{ m_1^2 c^4 + c^2 \right\} \sum_{i=2}^{N+1} K'_{i\perp} - \frac{q_1 \hbar}{c} \beta_1 \tau_{1z} - \mu_{\text{ano}}(1) \beta_1 \tau_{1z} + c^2 \left[\sum_{i=2}^{N+1} p'_{iz} \right] \right|^{1/2}$$

and

$$h_T(i) = \beta_i \left\{ m_e^2 c^4 + c^2 \left(\pi_{i\perp}^{\prime 2} - \frac{\theta \hbar}{c} \beta \tau_{iz} \right) \right\}^{1/2} - \mu_{\text{ano}}(i) \beta \tau_{iz} + c^2 p_{iz}^{\prime 2} \quad (13)$$

where the τ 's are Pauli spin matrices. The transformed Dirac operators $h_T(i)$ are manifestly separable. To obtain their eigenvalues, one needs to substitute the eigenvalues of the z components individual mechanical momentum and of τ_{iz} in the above [2].

The above process also transforms the interaction operator. The odd terms in the transformed interaction can be removed by a series of Foldy-Wouthuysen type of transformations. The final form of the interaction operator becomes

$$U'_{\text{res}} = U_{\text{Bee}} + U_{\text{Darwin}} + U'_{\text{Darwin}} + U_{\text{spin-orbit}} + U'_{\text{spin-orbit}} + U_{\text{correction}} + U_{\text{hyperfine}} + U_{\text{contact interaction}} + U'_{\text{hyperfine}} \quad (14)$$

The components of the above interaction operator are explicitly given by

$$U_{\text{Bee}} = -Ze^2 \sum_i' r_i^{\prime -1} + e^2 \sum_{i<j}' r_{ij}^{\prime -1}, \quad (q_1 = -Ze)$$

$$U_{\text{Darwin}} = \frac{Z\pi e^2 \hbar^2 (1 + 2\mu_e)}{2m_e^2 c^2} \sum_i' \delta^3(r_i')$$

$$\frac{\pi e^2 \hbar^2 (1 + 2\mu_e)}{m_e^2 c^2} \sum_i' \sum_{j(>i)} \delta^3(r_j'),$$

$$U'_{\text{Darwin}} = \frac{Z\pi e^2 \hbar^2 (1 + 2\mu_1)}{2M^2 c^2} \sum_i' \delta^3(r_i'),$$

$$U_{\text{spin-orbit}} = \frac{Ze^2 \hbar (1 + 2\mu_e)}{4m_e^2 c^2} \sum_i' \sigma_i \cdot \frac{r_i'}{r_i'^3} \times p_i' + \frac{Ze^2 \hbar (1 + \mu_e)}{2Mm_e c^2} \sum_i' \sigma_i \cdot \frac{r_i'}{r_i'^3} \times \sum_j' p_j'$$

$$U'_{\text{spin-orbit}} = \frac{e^2 \hbar (1 + 2\mu_e)}{4m_e^2 c^2} \sum_i' \sum_{j(\neq i)}' \sigma_i \cdot \frac{r_j'}{r_j'^3} \times p_j' + \frac{e^2 \hbar (1 + \mu_e)}{2m_e^2 c^2} \sum_i' \sum_{j(\neq i)}' \sigma_i \cdot \frac{r_j'}{r_j'^3} \times p_j'$$

$$\begin{aligned}
U_{\text{correction}} &= -\frac{Ze^2}{2Mm_e c^2} \sum_i' \sum_j' \left\{ \frac{1}{r_i'} \mathbf{p}_i' \cdot \mathbf{p}_j' + \frac{1}{r_i'^3} \mathbf{r}_i' (\mathbf{r}_i' \cdot \mathbf{p}_j') \cdot \mathbf{p}_i' \right\} \\
&\quad - \frac{e^2}{2m_e^2 c^2} \sum_i' \sum_{j(>i)} \left\{ \frac{1}{r_{ij}'} \mathbf{p}_i' \cdot \mathbf{p}_j' + \frac{1}{r_{ij}'^3} \mathbf{r}_{ij}' (\mathbf{r}_{ij}' \cdot \mathbf{p}_j') \cdot \mathbf{p}_i' \right\}, \\
U_{\text{hyperfine}} &= \frac{e^2 \hbar^2 (1 + \mu_e)^2}{4m_e^2 c^2} \sum_i' \sum_{j(>i)} \left\{ \frac{\sigma_i \cdot \sigma_j}{r_{ij}'^3} - 3 \frac{\sigma_i \cdot \mathbf{r}_{ij}' \sigma_j \cdot \mathbf{r}_{ij}'}{r_{ij}'^5} \right\}, \\
U_{\text{contact interaction}} &= -\frac{2\pi e^2 \hbar^2 (1 + \mu_e)^2}{3m_e^2 c^2} \sum_i' \sum_{j(>i)} \sigma_i \cdot \sigma_j \delta^3(\mathbf{r}_{ij}'), \\
U'_{\text{hyperfine}} &= -\frac{Ze^2 \hbar^2 (1 + \mu_1)(1 + \mu_e)}{4Mm_e c^2} \sum_i' \left\{ \frac{\sigma_i \cdot \sigma_i}{r_i'^3} - 3 \frac{\sigma_i \cdot \mathbf{r}_i' \sigma_i \cdot \mathbf{r}_i'}{r_i'^5} - \frac{8\pi}{3} \sigma_i \cdot \sigma_i \delta^3(\mathbf{r}_i') \right\} \\
&\quad + \frac{Ze^2 \hbar}{4c^2} \left(\frac{1 + 2\mu_1}{M^2} + \frac{2(1 + \mu_1)}{Mm_e} \right) \sigma_1 \cdot \sum_i' \frac{\mathbf{r}_i'}{r_i'^3} \times \mathbf{p}_i' + \frac{Ze^2 \hbar}{4M^2 c^2} \sigma_1 \cdot \sum_i' \frac{\mathbf{r}_i'}{r_i'^3} \times \sum_{j(1)}' \mathbf{p}_j'. \quad (15)
\end{aligned}$$

The prime on each summation sign indicates that summations are taken for $i = 2, \dots, N + 1$. The genesis of the above terms is very clear from this treatment that is discussed in detail in Ref. [4]. Most of these terms are well known. However, the third and the last term in the above, U'_{Darwin} and $U'_{\text{Hypertfine}}$, are not commonly encountered in the literature, are lower than the respective unprimed terms by factors of m_e^2/M^2 and m_e/M respectively, and will need attention as more powerful experimental techniques develop.

4. Discussion

Most of the systems of interest in Chemistry are weakly relativistic. With a few exceptions like nuclear spins that control NMR, and X-ray spectroscopy, most of the chemical effects are in the non-relativistic limits. Therefore, one would like to know the non-relativistic limit of the transformed Hamiltonian.

The Hamiltonian in the non-relativistic limit is obtained by expanding the one-particle operators $h_T(i)$'s through order v^2/c^2 , and replacing the transformed Casimir projection operators by unit operators. We get

$$H_{\text{nonrel}} = W_{\text{Sch}} + \Delta W_{\text{Sch}} + W_{\text{Epr}} + \Delta W_{\text{Epr}} + W_{\text{Nmr}} + W_{\text{rel}} + U'_{\text{res}}. \quad (16)$$

In the non-relativistic Hamiltonian, W_{Sch} is the Schrödinger free-particle Hamiltonian, and

ΔW_{Sch} is a corrective term due to the nuclear recoil, W_{Epr} is the interaction of the magnetic field with the total orbital angular momentum and the total spin angular momentum of the electrons and the diamagnetic interactions, the term ΔW_{Epr} represents the interaction of the orbital angular momentum of the recoiling nucleus with the magnetic field. The term W_{Nmr} is for the energy of interaction of the nuclear spin magnetic moment and the magnetic field, and W_{rel} is the kinetic energy corrections. These contributions, are explicitly written as

$$W_{\text{Sch}} = \frac{1}{2m_{\text{red}}} \sum_i' p_i'^2 - Ze^2 \sum_i' r_i'^{-1}.$$

$$\Delta W_{\text{Sch}} = \frac{1}{2M} \sum_i' \sum_{j(\neq i)}' k_i' \cdot k_j',$$

$$W_{\text{Epr}} = -\frac{e}{2m_e c} \mathbf{B} \cdot [\mathbf{L} + 2(1 + \mu_e)\mathbf{S}] + \frac{e^2 B^2}{8m_{\text{red}} c^2} \sum_i' r_{i\perp}^2, \quad (17)$$

$$\Delta W_{\text{Epr}} = \frac{e}{2Mc} \mathbf{B} \cdot \mathbf{L},$$

$$W_{\text{Nmr}} = \frac{Ze(1 + \mu_1)}{Mc} \mathbf{B} \cdot \mathbf{I},$$

$$W_{\text{rel}} = -\sum_i' \frac{p_i'^4}{8m_e^3 c^2} - \frac{1}{8M^3 c^2} \left(\sum_i' p_i' \right)^4.$$

Here, \mathbf{L} and \mathbf{S} are the total orbital angular momentum and the total spin angular momentum operators for the electrons, and \mathbf{I} is the spin angular momentum operator for the nucleus.

This theory has the following accomplishments : (1) The nuclear magnetic resonance and electron paramagnetic resonance interaction terms have been derived here from the appropriate relativistic Hamiltonian for an all-fermion atom placed in a homogeneous magnetic field. (2) The correction term to electron paramagnetic resonance is generally not considered in literature. However, its effect would be of the order of hyperfine interactions and hence must be accounted for in an accurate analysis of the EPR spectrum. (3) Its effect should also be detected in NMR spectroscopy for a $L \neq 0$ atom.

As a whole, we observe that Tsai and Weaver transformations can be systematically applied to derive the N-electron Hamiltonian for an atom with a spin-1/2 nucleus. It is possible to rigorously derive the transformed Hamiltonian which is separable for individual positive- and negative-energy states for all the particles, specifically here through order v^2/c^2 in interaction. The non-relativistic limit of the

transformed Hamiltonian is easily calculated. From this, the origin of the electronic and magnetic resonance spectroscopies can be explained.

Although the treatment here is for an all-fermion atom, it can easily be extended to the treatment of a molecule containing only the spin- $\frac{1}{2}$ nuclei. In the latter case, particles 2, 3, etc. will be considered as nuclei, and the rest as electrons. The center of mass needs to be redefined. The operator W_{Sch} has to be modified, and one will have to apply a careful accounting of the dynamics while taking the Born-Oppenheimer approximation and the non-adiabatic coupling into considerations. This part of the work remains to be done.

We have recently derived the expression for the retarded interaction between a spin-0 boson and a spin- $\frac{1}{2}$ fermion [12]. This derivation opens up the possibility of writing the Hamiltonian operator for a general molecule that consists of spin-0 and spin- $\frac{1}{2}$ nuclei, like carbon, oxygen, and of course, hydrogen.

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References

- [1] S N Datta and A Misra *J. Chem. Phys.* **114** 1478 (2001); *ibid.* **114** 9209 (2001)
- [2] S N Datta and A Misra *Int. J. Quantum Chem.* **82** 209 (2001)
- [3] S N Datta and A Misra *Int. J. Quantum Chem.* **90** 812 (2002)
- [4] A Misra and S N Datta *J. Chem. Phys.* **123** 064101 (2005)
- [5] J Sucher *Phys. Rev.* **A22** 348 (1980)
- [6] I Lindgren, S Salomonson and B Åsén *Phys. Reports* **389** 161 (2004); I Lindgren, S Salomonson and D Hedendahl *Phys. Rev.* **A73** 056501 (2006)
- [7] E E Salpeter and H A Bethe *Phys. Rev.* **84** 1232 (1951)
- [8] W A Barker and F N Glover *Phys. Rev.* **99** 317 (1955)
- [9] J E Avron, I W Herbst and B Simon *Ann. Phys. (New York)* **114** 431 (1978)
- [10] W Tsai *Phys. Rev.* **D7** 1945 (1973)
- [11] D L Weaver *J. Math. Phys.* **18** 306 (1977)
- [12] S N Datta and A Misra *J. Chem. Phys.* **125** 084111 (2006)