1. Atomic Theory in External Electric and Magnetic Fields

The magnetic fields we are concerned with, 10^5–10^8 G, and the associated electric fields either intrinsic to mCVs or the motion-induced Lorentz fields, are considered to be in the weak-field regime, in the sense that the Zeeman and Stark energy splitting of atomic ions is much smaller than the Coulomb interaction between the electrons and the nucleus. However, the magnitude of electron-electron correlation energies may be comparable or even smaller than the interaction with the external fields. Therefore, the two effects must be taken into account in the theoretical treatment with the same level of detail. The natural method of solving this problem is the configuration interaction approximation, where the effects of both electron correlation and interaction with the external fields are included in all order within a limited configuration space.

For atomic ions in a field-free environment, the total angular momentum, J, and parity, π, are good quantum numbers. Therefore, the total Hamiltonian is block diagonal when basis states of definite $J\pi$ symmetries are used. The magnetic field breaks the spherical symmetry, although π and the angular momentum projection on the field direction are still conserved. The electric field in a direction different from that of the magnetic field further destroys the cylindrical and mirror symmetries, and no quantum number other than the energy can be considered conserved. The Hamiltonian matrix in the external fields is therefore typically much larger than in the zero-field case.

Relativistic effects can be important for highly charged ions of interest in this study, and we will start from the Dirac Hamiltonian to solve the atomic structure

$$H = H_0 + H_B^{(1)} + H_B^{(2)} + H_E, \tag{1}$$

where

$$\begin{aligned} H_B^{(1)} &= \sum_i \mu_B \left(2\vec{S}_i + \vec{L}_i\right) \cdot \vec{B} \\ H_B^{(2)} &= \sum_i \frac{1}{2}\mu_B^2 \left|\vec{B} \times \vec{r}_i\right|^2 \\ H_E &= \sum_i \vec{E} \cdot \vec{r}_i. \end{aligned} \tag{2}$$

The summation in the above equations is over all electrons, H_0 is the field-free Hamiltonian, $H_B^{(1)}$ is the linear Zeeman term, $H_B^{(2)}$ is the diamagnetic Zeeman term, H_E is the interaction with the electric field, $\vec{S}_i$, $\vec{L}_i$, $\vec{r}_i$, are the spin angular momentum, orbital angular momentum, and position operators of the i-th electron, $\mu_B = 5.788 \times 10^{-5}$ eV/T is the Bohr magneton, and $\vec{E}$ and $\vec{B}$ are the electric and magnetic field vectors.

In the configuration interaction approximation, the wavefunction of the system is assumed to be $\psi = \sum_i b_i \phi_i$, where ϕ_i is the antisymmetrized product of single-electron Dirac

wavefunctions for any given electronic configuration. These single-electron wavefunctions are normally derived from self-consistent Dirac-Fock calculations without consideration of external fields. The mixing coefficients, b_i, and the energy value associated with the total wavefunction ψ are the eigenvalue solution of the Hamiltonian matrix in the representation of ϕ_i basis. The matrix elements of the Hamiltonian are given by $H_{ij} =< \phi_i|H|\phi_j >$.

The first step in solving the atomic structure is therefore to construct the Hamiltonian matrix with a suitable set of basis wavefunctions. Because we are only concerned with the weak-field regime in this project, the basis wavefunctions are derived using the same method used as in the zero-field approximation. In particular, we will make use of the existing Flexible Atomic Code (FAC, see §**??** for more details) as a general framework, within which the new atomic theory will be implemented. The calculation of Hamiltonian matrix elements of H_0 is also the same as in the zero-field case. Therefore, we will only need to develop new codes to obtain matrix elements of $H_B^{(1)}$, $H_B^{(2)}$, and H_E. These matrix elements are more easily calculated by converting the vector products into spherical tensor form, and separating the radial and angular integrations using the angular momentum theory.

Using the spherical tensor components of a vector

$$\begin{aligned} T_1 &= -\frac{1}{\sqrt{2}}\left(V_x + iV_y\right) \\ T_0 &= V_z \\ T_{-1} &= \frac{1}{\sqrt{2}}\left(V_x - iV_y\right). \end{aligned} \tag{3}$$

The H_E term is rewritten as

$$\begin{aligned} H_E &= \sum_q (-1)^q E_q r_i C^1_{-q}(i) \\ &= \sum_q (-1)^q E_q \sum_{\alpha\beta} Z^1_{-q}(\alpha\beta) < \alpha||C^1||\beta > r, \end{aligned} \tag{4}$$

where $q = -1$,0, or 1, C^k_q is the normalized spherical harmonics defined as

$$C^k_q = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_{kq}(\theta,\phi), \tag{5}$$

and $Z^k_q(\alpha\beta)$ is the second quantized form of the angular operator, and α and β are the single-electron Dirac orbitals present in the basis states. The reduced matrix elements of C^k are given by

$$< \alpha||C^k||\beta >= (-1)^{j_\alpha+1/2}\left[(2j_\alpha+1)(2j_\beta+1)\right]^{1/2} \begin{pmatrix} j_\alpha & k & j_\beta \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix}, \tag{6}$$

where $\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ represents the Wigner $3j$ symbol. This standard way of separating radial and angular integration is used throughout FAC to compute matrix elements of various operators, including, but not limited to, the Hamiltonian.

After some algebraic manipulation, the angular reduction of the $H_B^{(1)}$ term results in

$$\begin{aligned} H_B^{(1)} &= \mu_B \sum_q (-1)^q B_q \sum_{\alpha\beta} Z^1_{-q}(\alpha\beta) < \alpha||J^1 + S^1||\beta > \\ &= \mu_B \sum_q (-1)^q B_q \sum_{\alpha\beta} Z^1_{-q}(\alpha\beta) \Bigg\{ \delta_{j_\alpha j_\beta} \left[j_\alpha (j_\alpha + 1)(2j_\alpha + 1) \right]^{1/2} \\ &+ (-1)^{j_\alpha + l_\alpha - 1/2} \left(\frac{3}{2} \right)^{1/2} \left[(2j_\alpha + 1)(2j_\beta + 1) \right]^{1/2} \begin{Bmatrix} l_\alpha & \frac{1}{2} & j_\alpha \\ 1 & j_\beta & \frac{1}{2} \end{Bmatrix} \Bigg\}, \end{aligned} \tag{7}$$

where l_α, j_α are the orbital and total angular momentum of the Dirac orbital α, and $\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$ represents the Wigner $6j$ symbol, which comes as part of the reduced matrix elements of the spin operator.

The reduction of the $H_B^{(2)}$ term is more complicated, as it involves the cross product, and the quadratic term causes a rank-2 tensor to appear in the expression. It can be shown that

$$\begin{aligned} H_B^{(2)} &= \sqrt{3}\mu_B^2 r^2 \sum_{q_1 p_1} \begin{pmatrix} 1 & 1 & 0 \\ q_1 & p_1 & 0 \end{pmatrix} B_{q_1} B_{p_1} \begin{Bmatrix} 1 & 1 & 0 \\ 1 & 1 & 1 \end{Bmatrix} \sum_{\alpha\beta} Z^0_0(\alpha\beta) < \alpha||C^0||\beta > \\ &- \sqrt{30}\mu_B^2 r^2 \sum_{q q_1 p1} \begin{pmatrix} 1 & 1 & 2 \\ q_1 & p_1 & q \end{pmatrix} B_{q_1} B_{p_1} \begin{Bmatrix} 1 & 1 & 2 \\ 1 & 1 & 1 \end{Bmatrix} \sum_{\alpha\beta} Z^2_q(\alpha\beta) < \alpha||C^2||\beta > . \end{aligned} \tag{8}$$

Using Equations 4, 7 and 8, the construction of the Hamiltonian matrix becomes a simple matter of evaluating the angular coefficients $< \phi_i | Z^k(\alpha\beta) | \phi_j >$ and the average values of the radial operators r and r^2. These quantities are already calculated in FAC in the zero-field atomic structure theory, and existing code can be used.

After the Hamiltonian matrix is constructed, a standard linear algebra algorithm is used to solve the eigenvalue problem to obtain the field-modified energy levels and mixing coefficients, b_i, of the wavefunctions.

The calculation of radiative transition rates proceeds as in the zero-field theory, except that the wavefunctions now do not have a definite total angular momentum and parity. For example, the line strength of E1 transitions can be calculated as

$$S_{fi} = \sum_M \left| \sum_{\mu\nu} b_{f\mu} b_{i\nu} \sum_{\alpha\beta} < \phi_\mu || Z^1_M(\alpha, \beta) || \phi_\nu >< \alpha || C^1 || \beta > M^1_{\alpha\beta} \right|^2 , \tag{9}$$

where $M^1_{\alpha\beta}$ is the radial part of the relativistic single-electron E1 transition operator, as defined by **?**. The oscillator strength and transition rates are proportional to the line strengths.

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