Many-body Methods in Atomic Physics

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Abstract
Two methods of atomic many-body theory are introduced. Our discussion is based on the relativistic formulation. First, we have the many-body perturbation theory (MBPT). Then, we discuss the configuration interaction (CI) method. We conclude our lecture with a sample MBPT calculation of excitation energy for the divalent ion, Phosphorus IV.
Many-body Perturbation Theory (MBPT)*

We begin with the Dirac equation

\[ H \Psi = E \Psi, \]

where

\[ H_0 = \sum_i \left( c\alpha \cdot p + \beta c^2 - \frac{Z}{r} + u(r) \right) \]

\[ V = -\sum_i u(r_i) + \sum_{i<j} \frac{1}{r_{ij}}. \]

Here, \( u(r) \) is the effective central potential. The Breit interaction can also be included in \( V \) to take account of magnetic interaction and retardation

\[ b_{ij} = -\frac{1}{2r_{ij}} \left[ \alpha_i \cdot \alpha_j + \frac{\left( \alpha_i \cdot r_{ij} \right) \left( \alpha_j \cdot r_{ij} \right)}{r_{ij}^2} \right], \]

if high-precision calculations are needed.

The 0th-order eigenvalue equation is

\[ H_0 \Phi^\beta = E_0^\beta \Phi^\beta, \]

*Atomic unit a.u. is adopted, except for Table 1, where energy is expressed in cm\(^{-1}\).
and the eigenfunctions and eigenvalues are

\[
\Phi^\beta = A\{\phi_i(1)\phi_j(2) \cdots \phi_v(N)\},
\]

\[
E_0^\beta = \sum_i^N \varepsilon_i,
\]

where \(A\) is the anti-symmetrization operator.
Dirac-Hartree-Fock (DHF) Solution

The DHF approximation is commonly employed to obtain the 0th-order wavefunctions and energies. We set $u(r) = u_{\text{DHF}}(r)$, where the DHF potential (non-local) operator is defined through its matrix elements between a complete set of orbitals

$$\langle i | u_{\text{DHF}} | j \rangle = \sum_{b}^{\text{occupied}} \langle i b | r_{12}^{-1} (1 - P_{12}) | j b \rangle.$$ 

It is convenient to define a DHF (one-electron) operator

$$h_{\text{DHF}} = c \alpha \cdot p + \beta c^2 - \frac{Z}{r} + u_{\text{DHF}}(r),$$

then the 0th-order Hamiltonian can be compactly expressed as

$$H_0 = \sum_{i}^{N} h_{\text{DHF}}(r_i).$$
Partitioning of Functional Space

\[ P = \sum_{\alpha} |\alpha\rangle \langle \alpha| \]

\[ Q = \sum_{\beta \neq \alpha} |\beta\rangle \langle \beta| = 1 - P. \]

Intermediate normalization is defined via

\[ \langle \Psi_0 | \Psi \rangle = 1. \]
Brillouin-Wigner (BW) Perturbation Expansion

First, we write the Dirac equation as

\[(E - H_0)Q\Psi = QV\Psi.\]

Then, we define an \(E\)-dependent resolvent \(T_E\), which commutes with \(Q\),

\[T_E(E - H_0) = Q.\]

Component of the wavefunction in \(Q\) space is

\[Q\Psi = T_EV\Psi.\]

The exact wavefunction written in terms of \(T_E\) is

\[\Psi = \Psi_0 + T_EV\Psi.\]

BW expansion – For wavefunction:

\[\Psi = (1 + T_EV + T_EV T_EV + \cdots )\Psi_0.\]

For wave operator:

\[\Omega_E = 1 + \frac{Q}{E - H_0}V + \frac{Q}{E - H_0}V \frac{Q}{E - H_0}V + \cdots .\]
For energy:

\[ E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots, \]

where

\[ E^{(0)} = E_0 = \langle \Psi_0 | H_0 | \Psi_0 \rangle \]
\[ E^{(n)} = \left\langle \Psi_0 | V | \Psi^{(n-1)} \right\rangle, \quad n \geq 1. \]

The resolvent in spectral-resolution form is

\[ T_E = T_E \sum_{\beta} |\beta\rangle \langle \beta| \]
\[ = \sum_{\beta \neq \alpha} \frac{|\beta\rangle \langle \beta|}{E - E_0^\beta}. \]

Low-order corrections for wavefunction and energy are

\[ \Psi^{(1)} = \sum_{\beta \neq \alpha} \frac{|\beta\rangle \langle \beta| V | \alpha\rangle}{E - E_0^\beta} \]
\[ \Psi^{(2)} = \sum_{\beta \neq \gamma \neq \alpha} \frac{|\beta\rangle \langle \beta| V | \gamma\rangle \langle \gamma| V | \alpha\rangle}{(E - E_0^\beta)(E - E_0^\gamma)}, \]
\[ E^{(1)} = \langle \alpha | V | \alpha \rangle \]
\[ E^{(2)} = \sum_{\beta \neq \alpha} \frac{\langle \alpha | V | \beta \rangle \langle \beta | V | \alpha \rangle}{E - E_0^\beta} \]
\[ E^{(3)} = \sum_{\beta \gamma \neq \alpha} \frac{\langle \alpha | V | \beta \rangle \langle \beta | V | \gamma \rangle \langle \gamma | V | \alpha \rangle}{(E - E_0^\beta) (E - E_0^\gamma)} \].
Green’s Function Operator

We consider an inhomogeneous equation

\[(E - H)\Psi(x) = \phi(x), \quad x = \text{all coordinates},\]

and define a general resolvent

\[T(z) = (z - H)^{-1}.\]

The true Green’s function operator is

\[G^+(\varepsilon) = (\varepsilon - H + i\eta)^{-1}, \quad \eta > 0.\]

The wavefunction is written formally as

\[\Psi(x) = \lim_{\eta \to 0} G^+(E)\phi(x).\]

Analogous with \(T_E\) is the “0th-order” Green’s function operator

\[G_0^+(\varepsilon) = (\varepsilon - H_0 + i\eta)^{-1}.\]

Using the identity

\[(\varepsilon - H_0 + i\eta) = (\varepsilon - H + i\eta) + V,\]

\(\dagger\) Green’s function operator is also called propagator.
we obtain the Dyson Equation

\[ G^+(\varepsilon) = G_0^+(\varepsilon) + G_0^+(\varepsilon)V G^+(\varepsilon). \]

The true Green’s function operator is then expanded as

\[
G^+(\varepsilon) = \sum_{n=0}^{\infty} \left[ G_0^+(\varepsilon) \prod_{i=1}^{n} V G_0^+(\varepsilon) \right].
\]

Relation between Green’s function operator and (BW) resolvent is

\[ T_E = QG_0^+(E). \]
Rayleigh-Schrödinger (RS) Perturbation Expansion

We consider a group of states satisfying the Dirac equation

\[ H \Psi^a = E^a \Psi^a, \quad a = 1, 2, \ldots, d. \]

Using the definition of the wave operator

\[ \mathcal{P} H \Omega \Psi_0^a = E^a \Psi_0^a, \]

we can define an effective Hamiltonian

\[ H_{\text{eff}} = \mathcal{P} H \Omega \mathcal{P}. \]
**Generalized Bloch Equation**

We then have an eigenvalue equation for $H_{\text{eff}}$:

$$H_{\text{eff}} \Psi_0^a = E^a \Psi_0^a.$$ 

The Bloch equation for complete degeneracy is

$$(E_0 - H_0) \Omega \mathbf{P} = V \Omega \mathbf{P} - \Omega \mathbf{P} V \Omega \mathbf{P},$$

and the Generalized Bloch equation is

$$[\Omega, H_0] \mathbf{P} = (V \Omega - \Omega \mathbf{P} V \Omega) \mathbf{P}.$$ 

For a completely-degenerate case, we are able to define an $E$-independent resolvent

$$T = \frac{Q}{E_0 - H_0}.$$
Wave Operator $\Omega$

Low-orders of the wave operator are

$$
\Omega^{(0)} P = P \\
\Omega^{(1)} P = \frac{Q}{E_0 - H_0} VP \\
\Omega^{(2)} P = \frac{Q}{E_0 - H_0} V \frac{Q}{E_0 - H_0} VP \\
- \left( \frac{Q}{E_0 - H_0} \right)^2 VPVP, \text{ etc.}
$$

For general, i.e. noncompletely-degenerate, systems, low-orders of the wave operator are given by

$$
\Omega^{(0)} P = P \\
\left[ \Omega^{(1)}, H_0 \right] P = QVP \\
\left[ \Omega^{(2)}, H_0 \right] P = QV\Omega^{(1)} P - \Omega^{(1)} PVP \\
\left[ \Omega^{(3)}, H_0 \right] P = QV\Omega^{(2)} P - \Omega^{(2)} PVP \\
- \Omega^{(1)} PV\Omega^{(1)} P, \text{ etc.}
$$
Eigenenergy

The exact energy using intermediate normalization is

\[ E^a = \langle \Psi_0^a | H | \Psi_0^a \rangle = E_0^a + \langle \Psi_0^a | V \Omega | \Psi_0^a \rangle. \]

Low-order corrections for the energy are

\[ E^{a,(1)} = \langle \Psi_0^a | V | \Psi_0^a \rangle \]
\[ E^{a,(2)} = \langle \Psi_0^a | V \Omega^{(1)} | \Psi_0^a \rangle \]
\[ E^{a,(3)} = \langle \Psi_0^a | V \Omega^{(2)} | \Psi_0^a \rangle, \quad \text{etc.} \]
Variational Method

We review the variational method briefly, before introducing the configuration interaction (CI) method in the next section. Let $E[\phi]$ be the functional

$$E[\phi] = \frac{\langle \phi | H | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\int \phi^\dagger H \phi d\tau}{\int \phi^\dagger \phi d\tau},$$

where $\phi$ is an arbitrary normalizable (square-integrable) function. In the relativistic formulation, the trial function $\phi$ is a two-component column vector. We expand $\phi$ as

$$\phi = \sum_n a_n \Psi_n,$$

where $\Psi_n$’s are the orthonormal eigenfunctions of $H$.

We find

$$E[\phi] = \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2}.$$

Subtracting the lowest eigenenergy $E_0$ from both sides gives a minimum principle for the ground-state energy

$$E_0 \leq E[\phi].$$
If the trial function $\phi$ is made orthogonal to energy eigenfunctions corresponding to eigenvalues $E_0, E_1, E_2, \ldots, E_i$ (in ascending order). We have the orthogonality conditions

$$\langle \Psi_n | \phi \rangle = 0, \quad n = 0, 1, \ldots, i.$$  

The functional then becomes

$$E[\phi] = \frac{\sum_{n=i+1} a_n^2 E_n}{\sum_{n=i+1} |a_n|^2}.$$  

Subtracting $E_{i+1}$ from both sides gives

$$E_{i+1} \leq E[\phi].$$

We usually only have approximations $\{\phi_n, \ n = 0, 1, \ldots, i\}$ for the eigenfunctions $\{\Psi_n, \ n = 0, 1, \ldots, i\}$, then the orthogonality conditions are not fulfilled exactly. Thus, the minimum principle for energy of the excited state does not hold. To take an example, suppose we have obtained a normalized wavefunction $\phi_0(\approx \Psi_0)$. For a trial function $\phi_1$ orthogonal to $\phi_0$, i.e. $\langle \phi_0 | \phi_1 \rangle = 0$, we can derive the relation (an exercise for students)

$$E_1 - \epsilon_0(E_1 - E_0) \leq E[\phi_1], \quad \text{where} \quad \epsilon_0 = 1 - |\langle \Psi_0 | \phi_0 \rangle|^2 > 0.$$  

In general, if $\phi_0$ is a good approximation to $\Psi_0$, the violation of $E_1 \leq E[\phi_1]$ will be mild, since $\epsilon_0$ will be small.
The minimum principle is the basis of the Rayleigh-Ritz variational method. First, we select a trial function $\phi$ which depends on a number of variational parameters, then this function is used to evaluate $E[\phi]$. After that, we minimize $E[\phi]$ with respect to the variational parameters. The resulting functional (energy) is the best approximation to the eigenenergy allowed by the form chosen for $\phi$. 
Configuration Interaction

Since the true state of an atomic system (atom or ion) contains contributions from more than one configuration, we construct a trial function (CI wavefunction) as a linear combination of configuration functions (Slater determinants)

$$\phi = \sum_{n=1}^{N} c_n \Phi_n,$$

where $\Phi_1, \Phi_2, \ldots, \Phi_N$ are linearly-independent determinants, corresponding to different occupation scheme, and $c_1, c_2, \ldots, c_N$ (called the mixing coefficients) the linear variational parameters. Only configuration functions having the same angular-momentum values as the state considered ($\phi$) can contribute to the expansion.

We find for the energy functional

$$E[\phi] = \sum_{n'=1}^{N} \sum_{n=1}^{N} c_{n'}^{*} c_n H_{n'n} \frac{c_{n'}^{*} c_n \Delta_{n'n}}{\sum_{n'=1}^{N} \sum_{n=1}^{N} c_{n'}^{*} c_n \Delta_{n'n}},$$

$$H_{n'n} = \langle \Phi_{n'} | H | \Phi_n \rangle$$

$$\Delta_{n'n} = \langle \Phi_{n'} | \Phi_n \rangle$$

$$= \delta_{n'n} \text{ if } \Phi_n \text{'s orthonormal.}$$
is referred to as the overlap matrix. To minimize $E[\phi]$, we rearrange its formula as

$$E[\phi] \sum_{n' = 1}^{N} c_{n'}^* c_n \Delta_{n' n} = \sum_{n' = 1}^{N} c_{n'}^* c_n H_{n' n}.$$ 

Setting

$$\frac{\partial E}{\partial c_n} = 0 \quad \text{or} \quad \frac{\partial E}{\partial c_{n'}^*} = 0,$$

for all $n$ (or $n'$), gives a set of $N$ homogeneous linear equations

$$\sum_{n = 1}^{N} (H_{n' n} - \Delta_{n' n} E) c_n = 0,$$

for $n' = 1, 2, \ldots, N$. To obtain a non-trivial solution, we require

$$\det(H_{n' n} - \Delta_{n' n} E) = 0 \quad \text{(secular equation)}.$$

Its solution set consists of $N$ energy values (written in ascending order) and $N$ mixing-coefficient vectors

$$E = E_{i-1} \quad \text{and} \quad c = (c_1, c_2, \ldots, c_N)_{i-1}, \quad i = 1, 2, \ldots, N,$$

where $E_0$ is an upper bound to the ground-state energy, and the other $E$’s are upper bounds to excited-state energies. The $c$’s (when combined with the configuration functions) give the corresponding approximate eigenfunctions of the system.
## MBPT Application—Divalent Ion

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Table 1: Comparison of excitation energies in cm$^{-1}$ for the P$^{3+}$ ion.
Results in Table 1 are obtained using the Rayleigh-Schrödinger perturbation expansion. Phosphorus IV (P\(^{3+}\)) is an Magnesium-like ion. Second-order Breit correction \(B^{(2)}\) and lowest-order Lamb shift \(E_{\text{Lamb}}\) are also evaluated. The maximum relative error for excitation energy through third order of MBPT, \(E_{\text{tot}}\), is less than 0.9%. Experimental energies are taken from the NIST’s online database: physics.nist.gov/PhysRefData/ASD/index.html.