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

$$\begin{aligned} H_0 &= \sum_i^N \left(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta c^2 - \frac{Z}{r} + u(r) \right)_i \\ V &= -\sum_i^N u(r_i) + \sum_{i<j}^N \frac{1}{r_{ij}}. \end{aligned}$$

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

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

if high-precision calculations are needed.

The 0th-order eigenvalue equation is

$$H_0 \Phi^\beta = E_0^\beta \Phi^\beta,$$

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*Atomic unit a.u. is adopted, except for Table 1, where energy is expressed in cm^{-1}.

and the eigenfunctions and eigenvalues are

$$\begin{aligned}
\Phi^{\beta} &= \mathbf{A}\{\phi_i(1)\phi_j(2)\cdots\phi_v(N)\}, \\
E_0^{\beta} &= \sum_{i}^{N} \varepsilon_i,
\end{aligned}$$

where $\mathbf{A}$ 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 $u(r) = u_{\mathsf{DHF}}(r)$, where the DHF potential (non-local) operator is defined through its matrix elements between a complete set of orbitals

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

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

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

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

$$H_0 = \sum_{i}^{N} h_{\mathsf{DHF}}(r_i).$$

Partitioning of Functional Space

$$\begin{aligned}\mathbf{P} &= \sum_{\alpha} |\alpha\rangle\langle\alpha| \\ \mathbf{Q} &= \sum_{\beta\neq\alpha} |\beta\rangle\langle\beta| = \mathbf{1}-\mathbf{P}.\end{aligned}$$

Intermediate normalization is defined via

$$\langle\Psi_0|\Psi\rangle = 1.$$

Brillouin-Wigner (BW) Perturbation Expansion

First, we write the Dirac equation as

$$(E - H_0)\mathbf{Q}\Psi = \mathbf{Q}V\Psi.$$

Then, we define an E-dependent resolvent T_E, which commutes with $\mathbf{Q}$,

$$T_E(E - H_0) = \mathbf{Q}.$$

Component of the wavefunction in Q space is

$$\mathbf{Q}\Psi = T_E V\Psi.$$

The exact wavefunction written in terms of T_E is

$$\Psi = \Psi_0 + T_E V\Psi.$$

BW expansion – For wavefunction:

$$\Psi = (1 + T_E V + T_E V T_E V + \cdots)\Psi_0.$$

For wave operator:

$$\Omega_E = 1 + \frac{\mathbf{Q}}{E - H_0}V + \frac{\mathbf{Q}}{E - H_0}V\frac{\mathbf{Q}}{E - H_0}V + \cdots .$$

For energy:

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

where

$$\begin{aligned} E^{(0)} &= E_0 = \langle \Psi_0 | H_0 | \Psi_0 \rangle \\ E^{(n)} &= \left\langle \Psi_0 | V | \Psi^{(n-1)} \right\rangle , \quad n \geq 1. \end{aligned}$$

The resolvent in spectral-resolution form is

$$\begin{aligned} T_E &= T_E \sum_{\beta} |\beta\rangle\langle\beta| \\ &= \sum_{\beta\neq\alpha} \frac{|\beta\rangle\langle\beta|}{E - E_0^{\beta}}. \end{aligned}$$

Low-order corrections for wavefunction and energy are

$$\begin{aligned} \Psi^{(1)} &= \sum_{\beta\neq\alpha} \frac{|\beta\rangle\langle\beta|V|\alpha\rangle}{E - E_0^{\beta}} \\ \Psi^{(2)} &= \sum_{\beta\gamma\neq\alpha} \frac{|\beta\rangle\langle\beta|V|\gamma\rangle\langle\gamma|V|\alpha\rangle}{(E - E_0^{\beta})(E - E_0^{\gamma})}, \end{aligned}$$

$$
\begin{aligned}
E^{(1)} &= \langle\alpha|V|\alpha\rangle \\
E^{(2)} &= \sum_{\beta\neq\alpha}\frac{\langle\alpha|V|\beta\rangle\langle\beta|V|\alpha\rangle}{E-E_0^{\beta}} \\
E^{(3)} &= \sum_{\beta\gamma\neq\alpha}\frac{\langle\alpha|V|\beta\rangle\langle\beta|V|\gamma\rangle\langle\gamma|V|\alpha\rangle}{\left(E-E_0^{\beta}\right)\left(E-E_0^{\gamma}\right)}.
\end{aligned}
$$

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

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

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

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

Using the identity

$$(\varepsilon - H_0 + \mathrm{i}\eta) = (\varepsilon - H + \mathrm{i}\eta) + V,$$

[†] 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

$$\begin{aligned} G^{+}(\varepsilon) &= G_0^{+}(\varepsilon) + G_0^{+}(\varepsilon) V G_0^{+}(\varepsilon) \\ &\quad + G_0^{+}(\varepsilon) V G_0^{+}(\varepsilon) V G_0^{+}(\varepsilon) + \cdots . \end{aligned}$$

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

$$T_E = \mathbf{Q} G_0^{+}(E).$$

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

$$\mathbf{P}H\Omega\Psi_0^a = E^a\Psi_0^a,$$

we can define an effective Hamiltonian

$$H_{\text{eff}} = \mathbf{P}H\Omega\mathbf{P}.$$

Generalized Bloch Equation

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

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

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

$$T = \frac{\mathbf{Q}}{E_0 - H_0}.$$

Wave Operator Ω

Low-orders of the wave operator are

$$\begin{aligned}
\Omega^{(0)}\mathbf{P} &= \mathbf{P} \\
\Omega^{(1)}\mathbf{P} &= \frac{\mathbf{Q}}{E_0 - H_0} V \mathbf{P} \\
\Omega^{(2)}\mathbf{P} &= \frac{\mathbf{Q}}{E_0 - H_0} V \frac{\mathbf{Q}}{E_0 - H_0} V \mathbf{P} \\
&\quad - \left(\frac{\mathbf{Q}}{E_0 - H_0} \right)^2 V \mathbf{P} V \mathbf{P}, \quad \text{etc.}
\end{aligned}$$

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

$$\begin{aligned}
\Omega^{(0)}\mathbf{P} &= \mathbf{P} \\
\left[\Omega^{(1)}, H_0\right] \mathbf{P} &= \mathbf{Q} V \mathbf{P} \\
\left[\Omega^{(2)}, H_0\right] \mathbf{P} &= \mathbf{Q} V \Omega^{(1)} \mathbf{P} - \Omega^{(1)} \mathbf{P} V \mathbf{P} \\
\left[\Omega^{(3)}, H_0\right] \mathbf{P} &= \mathbf{Q} V \Omega^{(2)} \mathbf{P} - \Omega^{(2)} \mathbf{P} V \mathbf{P} \\
&\quad - \Omega^{(1)} \mathbf{P} V \Omega^{(1)} \mathbf{P}, \quad \text{etc.}
\end{aligned}$$

Eigenenergy

The exact energy using intermediate normalization is

$$E^a = \langle \Psi_0^a | H | \Psi^a \rangle = E_0^a + \langle \Psi_0^a | V\Omega | \Psi_0^a \rangle.$$

Low-order corrections for the energy are

$$\begin{aligned} E^{a,(1)} &= \langle \Psi_0^a | V | \Psi_0^a \rangle \\ E^{a,(2)} &= \left\langle \Psi_0^a \middle| V\Omega^{(1)} \middle| \Psi_0^a \right\rangle \\ E^{a,(3)} &= \left\langle \Psi_0^a \middle| V\Omega^{(2)} \middle| \Psi_0^a \right\rangle, \quad \text{etc.} \end{aligned}$$

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

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

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

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

where Ψ_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 ϕ 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

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

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 ϕ_1 orthogonal to ϕ_0, i.e. $\langle \phi_0 | \phi_1 \rangle = 0$, we can derive the relation (an exercise for students)

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

In general, if ϕ_0 is a good approximation to Ψ_0, the violation of $E_1 \le E[\phi_1]$ will be mild, since ϵ_0 will be small.

The minimum principle is the basis of the Rayleigh-Ritz variational method. First, we select a trial function ϕ 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 ϕ.

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 (ϕ) can contribute to the expansion.

We find for the energy functional

$$\begin{aligned} E[\phi] &= \frac{\sum_{n'=1 \atop n=1}^{N} c_{n'}^* c_n H_{n'n}}{\sum_{n'=1 \atop n=1}^{N} c_{n'}^* c_n \Delta_{n'n}}, \\ H_{n'n} &= \langle \Phi_{n'} | H | \Phi_n \rangle \\ \Delta_{n'n} &= \langle \Phi_{n'} | \Phi_n \rangle \\ &= \delta_{n'n} \quad \text{if } \Phi_n\text{'s orthonormal.} \end{aligned}$$

Δ is referred to as the overlap matrix. To minimize $E[\phi]$, we rearrange its formula as

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

Setting

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

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

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

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 $\mathbf{c}$'s (when combined with the configuration functions) give the corresponding approximate eigenfunctions of the system.

MBPT Application–Divalent Ion

	$(3s3p)\ {}^3P_0$	$(3s3p)\ {}^3P_1$	$(3s3p)\ {}^3P_2$
$E^{(0+1)}$	67021.3	67242.9	67696.5
$E^{(2)}$	110.3	116.0	130.1
$B^{(2)}$	-0.9	0.3	1.3
$E^{(3)}$	807.4	807.6	807.6
E_{Lamb}	-21.1	-20.9	-20.5
E_{tot}	67917.1	68146.0	68615.0
E_{expt}	67918.0	68146.5	68615.2
ΔE	-0.9	-0.5	-0.2
	$(3s3p)\ {}^1P_1$	$\left(3p^2\right)\ {}^1D_2$	$\left(3p^2\right)\ {}^3P_0$
$E^{(0+1)}$	120479.5	180554.7	165971.6
$E^{(2)}$	-20906.0	-61699.8	-2027.7
$B^{(2)}$	-15.8	-8.4	-5.2
$E^{(3)}$	6470.7	48769.6	1089.6
E_{Lamb}	-20.7	-43.6	-44.0
E_{tot}	106007.7	167572.4	164984.3
E_{expt}	105190.4	166144.0	164941.4
ΔE	817	1428	43
	$\left(3p^2\right)\ {}^3P_1$	$\left(3p^2\right)\ {}^3P_2$	$\left(3p^2\right)\ {}^1S_0$
$E^{(0+1)}$	166200.8	166633.3	212201.4
$E^{(2)}$	-2013.9	-2008.1	-23060.7
$B^{(2)}$	-4.8	-2.7	-24.6
$E^{(3)}$	1087.9	1077.3	5810.7
E_{Lamb}	-43.8	-43.4	-41.3
E_{tot}	165226.1	165656.5	194885.6
E_{expt}	165185.4	165654.0	194591.8
ΔE	41	3	294

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 $\left(\mathrm{P}^{3+}\right)$ is an Magnesium-like ion. Second-order Breit correction $B^{(2)}$ and lowest-order Lamb shift E_{Lamb} are also evaluated. The maximum relative error for excitation energy through third order of MBPT, E_{tot}, is less then 0.9%. Experimental energies are taken from the NIST's online database: physics.nist.gov/PhysRefData/ASD/index.html.