Calculations of energy levels for atoms with several valence electrons

V. A. Dzuba and V. V. Flambaum

University of New South Wales, School of Physics, 2052 Sydney, Australia

M. G. Kozlov[a)]

St. Petersburg Nuclear Physics Institute, Russian Academy of Sciences, 188350 Gatchina, Russia

A new *ab initio* method for doing high-accuracy calculations for atoms with more than one valence electron is described. An effective Hamiltonian for the valence electrons is formed using many body perturbation theory for the residual core–valence interaction. The configuration interaction method is used then to find the energy levels of the atom. Application to thallium shows that this method gives an accuracy of about 0.5% for the ionization potential and a few tenths of a percent for the first few energy intervals. © *1996 American Institute of Physics.* [S0021-3640(96)00411-2]

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The development of new methods for high-accuracy atomic calculations is necessary not only for atomic physics itself, but also for application of the methods of atomic physics to investigation of the fundamental interactions (see, for example, Refs. 1–4). At present, the 1% accuracy level has been reached in several measurements of parity nonconservation (PNC) in cesium,[5] lead,[6] thallium,[7] and bismuth.[8] But until now the same theoretical accuracy has been reached only for cesium[9,10] and francium.[11] All these calculations were made with the many body perturbation theory (MBPT).[12] Direct application of the MBPT to other heavy atoms can not guarantee the same accuracy because the electrostatic interaction between valence electrons is not small. On the other hand, the configuration interaction (CI) method can be very effective in treating a few-body problem with a small number of particles. But the CI method does not make allowance for the core–valence correlations.

It is natural to try to combine the two methods in an attempt to reach high accuracy for atoms with more than one valence electron. Here we describe a method which uses MBPT to construct the generalized self-energy operator Σ in the subspace corresponding to the valence electrons. This operator includes both a one-particle part and a part which takes into account the screening of the Coulomb interaction between valence electrons. It is added to the CI Hamiltonian before the eigenvalue problem is solved.

In this paper we focus on the calculation of energy levels, but the method can be extended to calculate transition amplitudes and expectation values. Our final goal is to calculate parity nonconserving $E1$ amplitudes for the atoms where precise PNC measurements are underway, i.e., thallium, lead, and bismuth.

The idea of the method is very simple. Electrons are divided into two groups, namely the core and the valence electrons. The effective Hamiltonian for the valence electrons is formed using the MBPT technique for the interaction of the valence electrons with the core. The CI method is used then to find the energy levels and the wave functions of the atom. Configurations with excitations from the core are not included explicitly on the CI stage. Here we give a very brief description of the method, leaving the details for a longer paper.

Let us divide the problem into a CI part and a MBPT part so that: i) no excitations from the core are included in the CI stage; ii) MBPT is applied only for processes in which at least one electron from the core is excited in each intermediate state. The effective Hamiltonian for the CI problem is formed using the well-known P,Q-formalism (see, for example, Ref. 12). Let us define the projector P on the many body states for which N_{core} electrons form the core. The orthogonal subspace corresponds to the projector $Q = 1 - P$. The CI Hamiltonian can be written as $H^{\text{CI}} = PHP$. In the pure CI method the following eigenvalue problem is solved:

$$H^{\text{CI}}\Phi_i^{\text{CI}} = E_i^{\text{CI}}\Phi_i^{\text{CI}}. \tag{1}$$

This equation is approximate, since it ignores the Q subspace. It is easy to write the exact equivalent of the Schrödinger equation in the P subspace. Let us make the P,Q-decomposition of the wave function of the many-body problem $\Psi = P\Psi + Q\Psi \equiv \Phi + \chi$. The equation $H\Psi_i = E_i\Psi_i$ corresponds to a system of equations for Φ_i and χ_i:

$$H^{\text{CI}}\Phi_i + PHQ\chi_i = E_i\Phi_i, \tag{2}$$

$$QHQ\chi_i + QHP\Phi_i = E_i\chi_i. \tag{3}$$

We can use Eq. (3) to eliminate χ_i. This gives us a Schrödinger-like equation in the P subspace with an energy-dependent effective Hamiltonian:

$$(H^{\text{CI}} + \Sigma(E_i))\Phi_i = E_i\Phi_i, \tag{4}$$

$$\Sigma(E) = PHQ \; R_Q(E) \; QHP, \tag{5}$$

where $R_Q(E) = (E - QHQ)^{-1}$. The orthonormality condition takes the form:

$$\langle\Phi_i|1 + PHQ \; R_Q(E_i) \; R_Q(E_k) \; QHP|\Phi_k\rangle = \delta_{i,k}. \tag{6}$$

Equations (4)–(6) are exact. If we are interested only in a few low-lying energy levels, we can neglect the energy dependence of the operators Σ and R_Q and evaluate both operators for some energy $E_{\text{av}} \simeq E_i \simeq E_k$. In this approximation Eq. (6) reduces to

$$\langle\Phi_i|1 - \partial_E\Sigma(E)|\Phi_k\rangle_{E=E_{\text{av}}} = \delta_{i,k}. \tag{7}$$

Note that if the CI subspace includes only one electron, then Σ is reduced to the one-particle self-energy operator, and Eqs. (4) and (7) define Bruckner orbitals. Thus, the operator Σ can be regarded as the direct generalization of the ordinary self-energy operator.

Now we need the perturbation theory expansion for (5). This expansion can be made most readily in the $V^{N_{\text{core}}}$ approximation, where $V^{N_{\text{core}}}$ is the Hartree–Fock field of the core. But for an atom with several valence electrons this field corresponds to a multiply
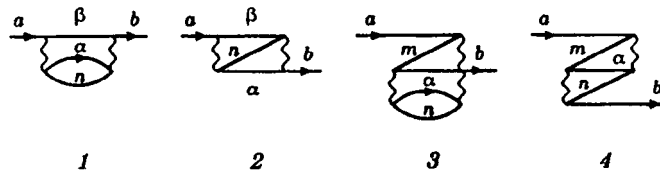
FIG. 1. Diagrams for the self-energy of the valence electron.

charged ion. It is therefore better to use a perturbation theory based on the $V^{N_{PT}}$ approximation, where N_{PT} can be chosen independently from the interval $N_{core} \leqslant N_{PT} \leqslant N$.

It can be shown that for the proper choice of the core orbitals, Eq. (5) is equivalent to

$$\Sigma(E) = P(V - V^{N_{PT}})Q \; R_Q(E) \; Q(V - V^{N_{PT}})P, \tag{8}$$

where V is the two-electron electrostatic interaction and $V^{N_{PT}}$ is the interaction with the Hartree–Fock field of the N_{PT} electrons. Now we can use the standard expansion for the operator $R_Q(E)$, treating $(V - V^{N_{PT}})$ as a perturbation. In the lowest order

$$R_Q(E) = Q(E - H_{DF})^{-1}Q, \tag{9}$$

where H_{DF} is the Dirac–Fock operator associated with the $V^{N_{PT}}$ field.

The operator Σ can be calculated with the help of Eqs. (8) and (9) within the standard diagrammatic technique. The projectors P and Q are taken into account by two simple rules: i) all external lines must be those of particles; ii) there should be at least one hole line in each intermediate state.

The perturbation expansion for Σ starts with the second order. The corresponding diagrams can have one, two, or three external lines. Diagrams of the first type describe corrections to the one-particle part of the CI Hamiltonian (Figs. 1 and 2). Diagrams of the second type give corrections to the two-particle interaction and are referred to as the screening corrections (Figs. 3 and 4). Diagrams of the third type correspond to an effective three-particle interaction and are negligible if the number of valence electrons is not too large.

For the case $N_{core} = N_{PT}$, only the diagrams in Figs. 1 and 3 exist. The additional diagrams shown in Figs. 2 and 4 take into account the fact that the Hartee–Fock field
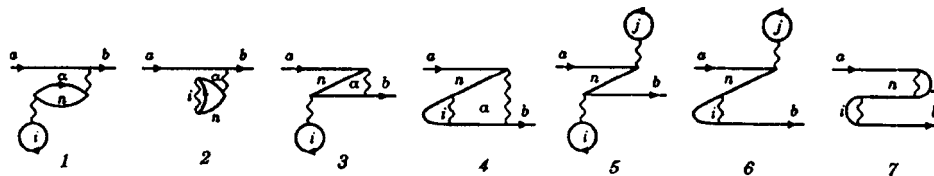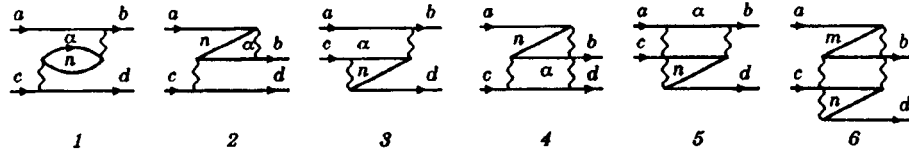

FIG. 2. Subtraction diagrams for the self-energy.

FIG. 3. Diagrams for screening.

includes contributions from $N_{\text{PT}}-N_{\text{core}}$ valence electrons. We call them subtraction diagrams because the Hartree–Fock field enters Eqs. (8) and (9) with a minus sign.

We have chosen thallium to test the method because it is the second simplest atom (after cesium) among those used in the ongoing PNC experiments. Thallium has the configuration $6s^2 6p$, and can be treated within MBPT as a one-electron atom;[13] however, the accuracy appears to be lower than for cesium. The main reason for this is the shallow shell $6s^2$ which strongly interacts with the $6p$ electron. Thus, we define the core as $[1s^2...5d^{10}]$, leaving three electrons in the CI space. Comparison of this core with the cores used in the MBPT calculations of Tl and Cs indicates that the core used here is likely to provide much better convergence of the MBPT. For example, the dipole polarizabilities of the three cores are 7, 24, and 17 a.u., respectively.

For the MBPT calculations of Σ the number of valence electrons is not fixed. The diagrammatic technique allows one to define Σ in terms of one-particle and two-particle radial integrals. Using these radial integrals, we can calculate the operator Σ for all possible valence configurations, including those which correspond to the ionized atom. Thus, we start with calculations for neutral thallium, and then use the same set of radial integrals in calculations for the ions Tl^+ and Tl^{++}.

For the MBPT part of the problem, we use the V^{N-1} approximation, which corresponds to the solution of the Dirac–Fock equations for the configuration $1s^2...5d^{10}6s^2$. This choice requires calculation of the subtraction diagrams, but gives better results for neutral Tl.

Results for several levels of Tl, Tl^+, and Tl^{++} are given in Table I. Note that the typical accuracy of the Dirac–Fock method is about 10%. The CI method improves the accuracy by a factor of two, while the combined CI+MBPT method leads to further improvement of about an order of magnitude.
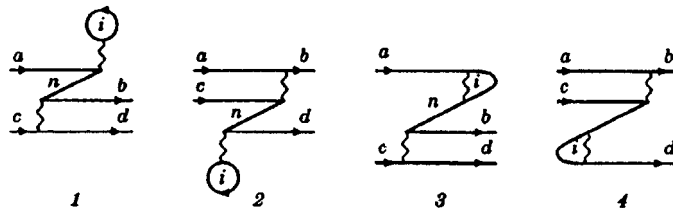

FIG. 4. Subtraction diagrams for screening.

TABLE I. Calculated binding energies for Tl, Tl^+, and Tl^{++} in comparison with experiment (cm^{-1}).

Ion	Config.	J	CI	CI+MBPT	Exper.[14,15]
Tl	$6s^2 6p$	1/2	46855	49507	49264
	$6s^2 6p$	3/2	39752	41655	41471
	$6s^2 7s$	1/2	21303	22459	22787
	$6s^2 7p$	1/2	13835	14726	15104
	$6s^2 7p$	3/2	12912	13726	14103
	$6s^2 6d$	3/2	7684	12940	13146
	$6s^2 6d$	5/2	7686	12867	13064
Tl^+	$6s^2$	0	156114	165379	164765
	$6s6p$	0	112380	115061	115314
	$6s6p$	1	109122	112271	112372
	$6s6p$	2	100295	102586	103040
	$6s6p$	1	81875	90726	89105
	$6s7s$	1	55957	58429	59540
	$6s7s$	0	53653	55537	56769
Tl^{++}	$6s$	1/2	232680	240681	240770
	$6p$	1/2	169981	177188	176614
	$6p$	3/2	155766	162264	161800
	$7s$	1/2	91702	100398	101561

In conclusion, we would like to stress that the proposed combination of many body perturbation theory and the CI method has a very convenient form. Since the diagrams are calculated in a one-electron basis, the whole method can be reduced to a redefinition of the one- and two-electron matrix elements of the ordinary CI Hamiltonian. The CI method itself remains almost untouched. It is possible to use a similar approach to calculate transition amplitudes. Core polarization effects can be taken into account with the help of the effective operators for the valence electrons.

[a] e-mail: kozlov@lnpi.spb.su

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