

# Combined configuration-superposition and many-particle perturbation calculations for atoms with two valence electrons

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A new high-precision method is used to calculate the characteristics of atoms with two valence electrons. An effective Hamiltonian for the valence electrons is formulated by many-particle perturbation theory with respect to the residual interaction of the valence electrons with the core. The configuration-superposition method is then used to find the energy levels of the atom. The application of the combined method to divalent calcium, strontium, barium, and ytterbium atoms shows that the ionization potential is obtained within 0.5% error limits. The precision attained for the first few lowest levels of the energy spectra is significantly higher than is obtained by configuration-superposition calculations alone. © 1997 American Institute of Physics. [S1063-7761(97)00603-3]

## 1. INTRODUCTION

The fruitfulness of atomic physics methods in the investigation of fundamental interactions is well known, especially in the study of discrete symmetries.<sup>1–4</sup> The nonconservation of parity has been measured to within 1% for a number of atoms.<sup>5–8</sup> However, only for cesium<sup>9,10</sup> and francium<sup>11</sup> has a comparable precision been attained in the calculations required for the interpretation of experiments. The need for a new method by which to improve the precision of atomic calculations is obvious in this light. This method, representing a combination of two well-known methods (the superposition of configurations and many-particle perturbation theory) was proposed earlier.<sup>12</sup>

The application of many-particle perturbation theory to heavy atoms with several valence electrons cannot be expected to yield high computational precision, because electrostatic interaction between valence electrons cannot be precisely accounted for within the context of this method. However, this situation can be rectified by the configuration-superposition method (or the related multiconfigurational Hartree–Fock method), which has been used on many occasions in calculations for complex atoms.<sup>13–20</sup> But then the precision of the configuration-superposition calculations is also limited by the impossibility of fully taking into account the correlations between core and valence electrons. These methods can therefore complement one another, and therein lies the motivation for their combining them.

## 2. BRIEF DESCRIPTION OF THE METHOD

The method has been proposed in two previous papers,<sup>12</sup> which include detailed descriptions. We shall therefore confine the present discussion to a review of its basic precepts. The complete Hilbert space, in which the many-particle Dirac equation

$$H\Psi = E\Psi \quad (1)$$

operates, is partitioned into two subspaces, and appropriate projection operators  $P$  and  $Q$  are introduced, satisfying the condition  $P + Q = 1$ . The Hamiltonian  $H$  and the wave function  $\Psi$  can be written as follows in the  $P, Q$  formalism:

$$H = PHP + PHQ + QHP + QHQ, \quad (2)$$

$$\Psi = P\Psi + Q\Psi \equiv \Phi + \chi. \quad (3)$$

The operator  $P$  is defined as the projector onto those states of the atom for which  $N_c$  electrons are always present in the core (i.e., the core does not contain any holes, as all  $N_c$  states are filled with electrons). The operator  $Q$  projects onto the orthogonal complement of subspace  $P$  (i.e., onto those states of the atom where at least one hole is present in the core).

The following problem is solved in the configuration-superposition stage:

$$(PHP)\Phi = E^C\Phi. \quad (4)$$

The solution of this equation is not a solution of Eq. (1), since the subspace  $Q$  is not taken into account here. It has been shown<sup>12</sup> that the inclusion of this subspace leads to the equations

$$[PHP + \Sigma(E)]\Phi = E\Phi, \quad (5)$$

$$\Sigma(E) = (PHQ) \frac{1}{E - QHQ} (QHP). \quad (6)$$

The normalization condition  $\langle \Psi_i | \Psi_k \rangle = \delta_{ik}$  can be rewritten in terms of the functions  $\Phi_i$  in the form

$$\langle \Phi_i | 1 + (PHQ) \frac{1}{E_i - QHQ} \frac{1}{E_k - QHQ} (QHP) | \Phi_k \rangle = \delta_{ik}. \quad (7)$$

If we restrict the discussion to a few of the lowest levels, i.e., if we assume that  $\Delta \equiv (E_i - E_k)/2$  is much smaller than  $E_{av} = (E_i + E_k)/2$ , we see at once that the second term in (7) can be written in the series form:

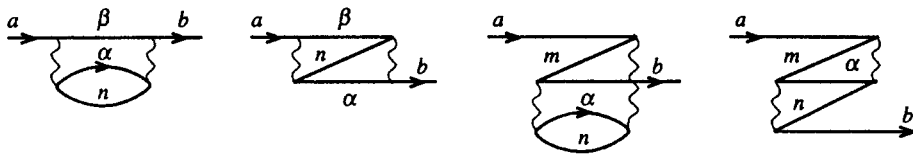


FIG. 1. Self-energy diagrams for valence electrons.

$$\begin{aligned}
 (PHQ) & \frac{1}{E_i - QHQ} \frac{1}{E_k - QHQ} (QHP) \\
 & = \left( -\frac{\partial \Sigma(E)}{\partial E} - \frac{\Delta^2}{6} \frac{\partial^3 \Sigma(E)}{\partial E^3} - \dots \right) \Bigg|_{E=E_0}. \quad (8)
 \end{aligned}$$

The first term of the expansion (8) is already much smaller than unity. Consequently, in calculating the lowest energy levels, we can simply omit the second term in Eq. (7) and write the normalization condition in the conventional form

$$\langle \Phi_i | \Phi_k \rangle = \delta_{ik}. \quad (9)$$

It has been shown<sup>12</sup> that the operator  $\Sigma(E)$  can be transformed as follows for the proper choice of core orbitals:

$$\Sigma(E) = P(V - V^{N_{PT}})Q \frac{1}{E - QHQ} Q(V - V^{N_{PT}})P, \quad (10)$$

where  $V$  denotes the two-electron electrostatic interaction, and  $V^{N_{PT}}$  is the interaction of  $N_{PT}$  electrons with the Hartree–Fock field. The quantity  $N_{PT}$  must satisfy the condition  $N_c \leq N_{PT} \leq N$ . For the calculation of the energy denominators in the indicated approximation  $E$  is replaced by  $E_{av}$  in Eq. (10).

The operator  $\Sigma$  is calculated by standard diagram technique. In the lowest order the corresponding diagrams can have one, two, or three outer lines.<sup>12</sup> Diagrams of the first type describe corrections to the one-electron part  $PHP$  (Figs. 1 and 2). Diagrams of the second type give a correction for shielding of the core by the interaction between valence electrons (Figs. 3 and 4). Diagrams corresponding to three-particle interaction, of course, do not exist for atoms with two valence electrons.

We note that the diagrams in Figs. 2 and 4 are drawn with allowance for the fact that the Hartree–Fock field includes contributions from  $N_{PT} - N_c$  valence electrons. They obviously vanish for the case  $N_{PT} = N_c$ . Since the potential  $V^{N_{PT}}$  occurs with a minus sign in Eq. (10), these diagrams are called subtractive.

### 3. COMPUTATIONAL PROCEDURE

The procedures used to perform the calculations can be divided into three parts. In the first stage a basis set of one-electron wave functions (orbitals) is formulated. The one-electron wave functions of the ground state of the atom and the corresponding one-electron energies are found by the Hartree–Fock–Dirac method. We use a program written by Brattsev, Deřneka, and Tupitsyn<sup>21</sup> and subsequently modified by Tupitsyn (in particular, with allowance for the finite size of the nucleus, which is important in the treatment of heavy atoms). In addition to the Hartree–Fock variety we also construct virtual orbitals. Each of these can be represented by the product of one of the corresponding orbitals of the same symmetry and the exponent  $r$  with subsequent orthogonalization of the newly constructed orbitals with respect to all those preceding. A similar method for the construction of basis functions has been proposed by Bogdanovich<sup>22,23</sup> and has already been used by us for calculations of ytterbium<sup>14</sup> and bismuth.<sup>15</sup>

In the second stage it is required to calculate the matrix elements of the operator  $\Sigma$ . To calculate the self-energy diagrams and the shielding diagrams by perturbation theory, we

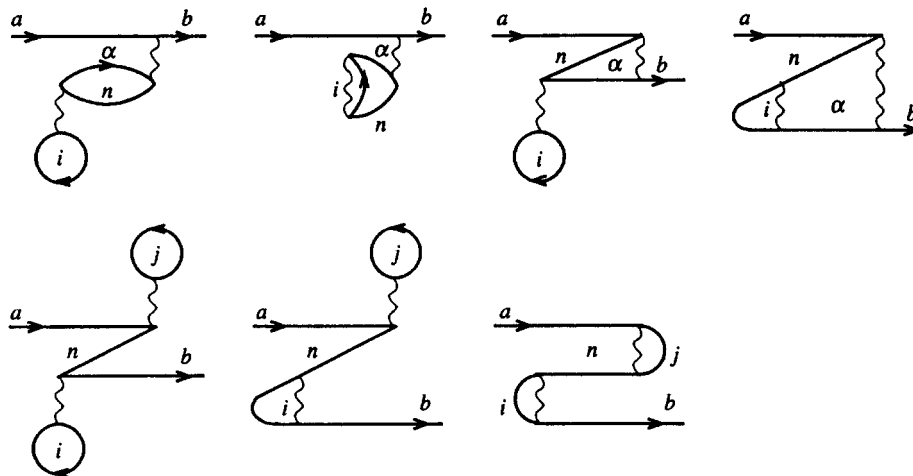


FIG. 2. Subtractive diagrams for the self-energy.

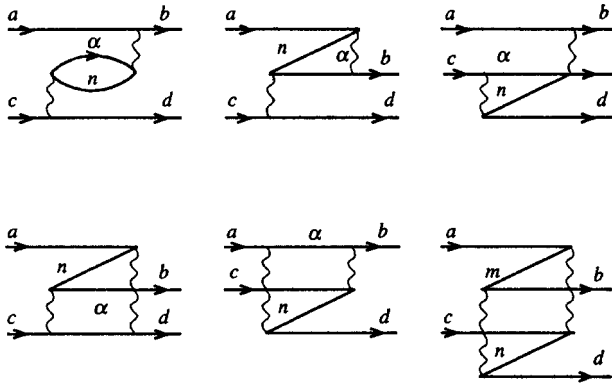


FIG. 3. Shielding diagrams.

use the constructed set of basis orbitals. Since we are concerned in this stage with the excitation of electrons having inner shells (which can be quite deeply situated), we must take into account a large number of states of the continuous spectrum as excited states. The need to include a large number of diagrams for a large number of excited states makes this part of the calculations the most time-consuming.

The third and final step is to solve Eq. (5). This can be done by the well-known configuration-superposition method. In the calculations we use a program written by Kotochigova and Tupitsyn,<sup>24</sup> which we have substantially modified.

#### 4. CALCULATIONS FOR Ca, Sr, Ba, AND Yb

We have chosen the Ca, Sr, Ba, and Yb atoms to test the configuration-superposition method in combination with many-particle perturbation theory. They have in common the existence of two *s*-electrons in the outermost shell. It is reasonable, therefore, to assume that *s*-electrons are present in the valence zone and that the remaining electrons form the core.

As mentioned, the first step in calculating the energy spectrum is to obtain the one-electron functions by the Hartree–Fock–Dirac method. In this stage a self-consistent field procedure is implemented for all electrons in the atom, including electrons of the outermost shell. The resulting orbitals are then frozen in place, one electron from the last *ns* shell is moved to the  $(n-1)d$  shell, and the Hartree–Fock–Dirac equation for this shell is solved ( $n=4,5$  for Ca and Sr, and  $n=6$  for Ba and Yb). The *np* shell is augmented analogously. The procedure culminates in the construction of Hartree–Fock orbitals for all electronic states of the main

configuration of atoms and also for the *np* and  $(n-1)d$  shells. The virtual orbitals, which together with the Hartree–Fock orbitals form the basis set, are subsequently constructed according to the procedure set forth in the preceding section. The number of orbitals that must be included in the basis will be discussed below.

The next stage is to calculate the matrix elements of the operator  $\Sigma$  by perturbation theory. In the case of the  $V^N$  approximation, which is the one used for the calculations, all the diagrams of Figs. 1–4 need to be taken into account (the subtractive diagrams do not vanish in this case, because  $N_{PT} \neq N_c$ ). In the perturbation calculations the number of excited states that must be included to attain saturation is fairly high. The test of whether saturation has been reached is that the matrix elements of the operator  $\Sigma$  essentially cease to change as new shells are added. For example, in the calculation of the energy spectrum of Yb, the following virtual states are included:  $7s-19s$ ,  $6p-19p$ ,  $5d-18d$ ,  $5f-17f$ ,  $5g-16g$ . The number of orbitals included for the other atoms is approximately the same. Once the virtual orbitals have been constructed, the Hartree–Fock–Dirac operator is diagonalized on them. In this case the majority of the orbitals of each symmetry resides in the continuous spectrum, and the energy of the last orbitals is on the order of  $10^2$  a.u.

Next we solve Eq. (5) by the configuration-superposition method, using the calculated matrix elements of the operator  $\Sigma$ . In this state we take into account configurations associated with the excitation of both valence (but not core!) electrons to higher levels. The configurations are augmented until the energy of the investigated levels no longer changes. (We assume that saturation is attained when the energy of the levels does not vary by more than  $30-40 \text{ cm}^{-1}$  with the addition of new configurations.) The basis set of orbitals required to attain saturation in the configuration-superposition calculations is far smaller than in the state where many-particle perturbation theory is used. In our case it is sufficient to include 18–27 virtual orbitals. The two or three highest *s*-, *p*-, *d*-, *f*- and *g*-shells are added as virtual. As explained, excitations in the *h*-shell are insignificant for the given atoms and can be disregarded.

For comparison we also solve Eq. (4) instead of (5) to obtain a solution by the pure configuration-superposition method. The results of calculations of the lowest energy levels for both methods, the pure configuration-superposition method (SC) and its coordination with the many-particle perturbation theory (SC+MPP) for the Ca, Sr, Ba, and Yb atoms are summarized in Tables I–IV.

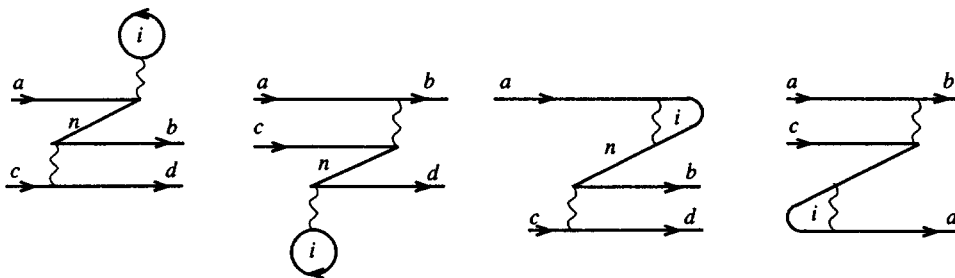


FIG. 4. Subtractive diagrams for shielding.

TABLE I. Energies of the lowest few levels of Ca ( $\text{cm}^{-1}$ ) (multiplet splittings are shown in parentheses).

Configuration	Level	SC	SC+MPP	Experiment <sup>25</sup>
$4s^2$	$^1S_0$	0	0	0
$4s4p$	$^3P_0^o$	13720	15230	15158
$4s4p$	$^3P_1^o$	13769 (49)	15284 (54)	15210 (52)
$4s4p$	$^3P_2^o$	13870 (101)	15394 (110)	15316 (106)
$4s3d$	$^3D_1$	23661	21489	20335
$4s3d$	$^3D_2$	23664 (3)	21505 (16)	20349 (14)
$4s3d$	$^3D_3$	23664 (0)	21530 (25)	20371 (22)
$4s3d$	$^1D_2$	23642	22984	21850
$4s4p$	$^1P_1^o$	23255	23555	23652

In addition to the energy spectra we can also calculate the ionization potentials of these atoms. Thus, in the case of two valence electrons their energy  $E_v$  is simply the sum of the first and second ionization potentials. Consequently, to find the first two ionization potentials, it is sufficient to also solve Eq. (5) for a single positive ion. If the same basis set of orbitals is used, the radial integrals needed in order to calculate the matrix elements of the operators  $H$  and  $\Sigma$  are the same as for the neutral atom. This fact is extremely important, since the calculation of the radial integrals for the operator  $\Sigma$  is the most costly operation in the computational sense. Knowing  $E_v$  for the atom and the ion, we can obtain the ionization potential for each of them without undue complication (see Tables V and Tables VI).

Analyzing the results obtained for the ionization potentials, we see that the combined method yields precision at the 0.5% level, which is roughly an order of magnitude better than obtained by pure configuration-superposition calculations. The energy spectrum obtained for the lower levels for all four atoms by the configuration-superposition method in conjunction with many-particle perturbation theory also exhibits significantly better agreement with the experimental. For odd levels the precision is close to that attained for the ionization potentials (i.e., for the most part better than 1%); for even levels (particularly the  $D$  levels) the precision is somewhat lower but still far better than for pure configuration-superposition calculations. The change in the multiplet splitting is especially dramatic when correlations are taken into account by perturbation theory. In the case of Yb, for example, it is evident from Table IV that the configuration-superposition method gives approximately one

TABLE II. Energies of several lowest levels of Sr ( $\text{cm}^{-1}$ ).

Configuration	Level	SC	SC+MPP	Experiment <sup>25</sup>
$5s^2$	$^1S_0$	0	0	0
$5s5p$	$^3P_0^o$	12475	14242	14318
$5s5p$	$^3P_1^o$	12648 (173)	14428 (186)	14504 (186)
$5s5p$	$^3P_2^o$	13007 (359)	14821 (393)	14899 (395)
$5s4d$	$^3D_1$	19618	18877	18159
$5s4d$	$^3D_2$	19635 (17)	18936 (59)	18219 (50)
$5s4d$	$^3D_3$	19664 (29)	19033 (97)	18319 (100)
$5s5p$	$^1P_1^o$	20863	21444	21698

TABLE III. Energies of several lowest levels of Ba ( $\text{cm}^{-1}$ ).

Configuration	Level	SC	SC+MPP	Experiment <sup>25</sup>
$6s^2$	$^1S_0$	0	0	0
$6s5d$	$^3D_1$	11019	9423	9034
$6s5d$	$^3D_2$	11104 (85)	9631 (208)	9216 (182)
$6s5d$	$^3D_3$	11281 (177)	10065 (434)	9597 (381)
$6s6p$	$^3P_0^o$	10253	12221	12266
$6s6p$	$^3P_1^o$	10597 (344)	12583 (362)	12637 (371)
$6s6p$	$^3P_2^o$	11370 (773)	13448 (865)	13515 (878)
$6s6p$	$^1P_1^o$	17157	17740	18060

tenth of the experimental splitting of the  $D$  triplet, whereas the combined method reproduces this splitting almost perfectly. The loss of precision for even as opposed to odd levels is most likely attributable to the fact that the Hartree–Fock  $d$ -functions are a poor approximation to the true wave functions. (We note that an attempt to use virtual rather than Hartree–Fock  $d$ -functions does nothing to improve the situation.)

## 5. CONCLUSION

Our calculations for atoms with two valence electrons (Ca, Sr, Ba, and Yb) by the combined method of configuration superposition and many-particle perturbation theory confirms that the accuracy of computation of such atomic characteristics as the ionization potential and the energy spectrum is significantly higher than when the pure configuration-superposition method is used. In particular, the ionization potential has been reproduced within 0.5% error limits.

Work is currently in progress on the application of the combined method for transition amplitude calculations. This approach will make it possible to improve the precision of calculation of impurity  $P$ -odd amplitudes needed for the interpretation of experimental parity-nonconservation results and for testing the standard model.

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TABLE IV. Energies of several lowest levels of Yb ( $\text{cm}^{-1}$ ).

Configuration	Level	SC	SC+MPP	Experiment <sup>25</sup>
$6s^2$	$^1S_0$	0	0	0
$6s6p$	$^3P_0^o$	14357	17075	17288
$6s6p$	$^3P_1^o$	15022 (665)	17764 (689)	17992 (704)
$6s6p$	$^3P_2^o$	16527 (505)	19447 (683)	19710 (718)
$6s5d$	$^3D_1$	25216	25075	24489
$6s5d$	$^3D_2$	25238 (22)	25338 (263)	24751 (262)
$6s5d$	$^3D_3$	25299 (61)	25855 (517)	25270 (519)
$6s6p$	$^1P_1^o$	24221	25306	25068

TABLE V. Ionization potentials of  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ , and  $\text{Yb}^+$  ( $\text{cm}^{-1}$ ).

Ion	SC	SC+MPP	Experiment
$\text{Ca}^+$	91887	95537	95748
$\text{Sr}^+$	84635	88747	88964
$\text{Ba}^+$	76011	80421	80687
$\text{Yb}^+$	90788	97254	98269

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TABLE VI. Ionization potentials of neutral atoms ( $\text{cm}^{-1}$ ).

Atom	SC	SC+MPP	Experiment
Ca	47806	49142	49305
Sr	44057	45679	45926
Ba	39881	41800	42032
Yb	46759	50295	50444

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