Combined CI+MBPT calculations of energy levels and transition amplitudes in Be, Mg, Ca, and Sr

I. M. Savukov and W. R. Johnson
Department of Physics, 225 Nieuwland Science Hall
University of Notre Dame, Notre Dame, IN 46566
(Dated: October 26, 2018)

Configuration interaction (CI) calculations in atoms with two valence electrons, carried out in the $V^{(N-2)}$ Hartree-Fock potential of the core, are corrected for core-valence interactions using many-body perturbation theory (MBPT). Two variants of the mixed CI+MBPT theory are described and applied to obtain energy levels and transition amplitudes for Be, Mg, Ca, and Sr.

PACS numbers: 31.10.+z, 31.25.-v, 32.30.-r, 32.70.-m

I. INTRODUCTION

Although Be, Mg, Ca, and Sr atoms have been studied theoretically for many years and numerous calculations are available in the literature, energy levels of those divalent atoms have been treated primarily with semiempirical methods and only a limited number of low-lying levels have been evaluated using ab-initio methods, which often do not provide sufficient precision or require extensive computer resources. Semiempirical methods, to their advantage, do not require significant computer resources and can be applied easily to a large number of levels; however, such theories have limited predictive power and accuracy. Although energies obtained using semiempirical methods agree well with one another and with experiment, oscillator strengths obtained by different semiempirical calculations are inconsistent. Examples of semiempirical calculations can be found for Be in [1], for Ca in [2], and for Sr in [3]. Large-scale ab-initio configuration interaction (CI) calculations of energies and transition rates, although capable of high accuracy, have been performed only for a few low-lying levels in the Be [4, 5] and Mg [6] isoelectronic sequences. The size of the configuration space in such CI calculations is limited by the available computer resources. Smaller-scale CI calculations, carried out in the frozen $V^{(N-2)}$ Hartree-Fock potential of the core, lead to poor results. We found, for example, that frozen-core CI calculations in Ca gave energies so inaccurate that it was difficult, if at all possible, to identify many closely spaced levels of experimental interest. Multi-configuration Dirac-Fock (MCDF) and Hartree-Fock (MCHF) methods have also been used to obtain energies and oscillator strengths in divalent atoms: MCHF for Be-like ions [7] and neutral calcium [8], and MCDF for Mg-like ions [9]. The accuracy of MCHF and MCDF calculations in neutral atoms is poor, basically because of computational limits on the number of configurations. Polarization potentials have been used in conjunction with MCHF calculations [10] to improve the accuracy of energies for Ca I and Ca II. Many-body perturbation theory (MBPT) calculations of energies and oscillator strengths for neutral divalent atoms using an effective Hamiltonian within a small model space, are also found to be inaccurate [11, 12]. Good agreement with experiment for divalent atoms, however, was achieved in Refs. [13, 14, 15] with a combined CI+MBPT method. A related method was applied to calculations of energies and oscillator strengths for Mg-like ions in Ref. [16]. Among the ab-initio methods, CI+MBPT is particularly attractive since it is capable of giving accurate energies and transition rates for both light and heavy divalent atoms with modest computer resources.

A precise and efficient theoretical method for calculations of properties of divalent atoms is needed for many possible applications of current interest, including calculations of spectra, transition amplitudes, hyperfine structure constants, polarizabilities, parity-nonconserving (PNC) amplitudes, van der Waals coefficients, and Lennard-Jones coefficients. There is also growing interest in properties of divalent atoms in conjunction with low-temperature Bose-Einstein condensation (BEC) experiments. For example, the prospect for achieving BEC in divalent atoms was discussed in [17, 18] and depends on the size of the van der Waals coefficient.

At least two major difficulties have been recognized in studying divalent atoms. First, core polarization effects are significant and must be taken into account. A similar situation exists in monovalent atoms where various methods have been successfully applied to describe the valence-core interaction. We have made extensive use of one of these methods, MBPT, and have developed methods for calculating all diagrams up to the third order for energies [19] and transition amplitudes [20]. A second major difficulty is that two valence electrons interact so strongly in neutral atoms that two-particle diagrams must be included to infinite order. Since infinite order is required, the MBPT method is difficult to apply. However, valence-valence correlations can be accounted for completely using the CI method.

With this in mind, we have developed a method (sim-
ilar to that used in Refs. [13, 14, 15] but with important differences for high-precision calculations of properties of atoms with two valence electrons. The method starts with a complete CI calculation of the interactions between the valence electrons in a frozen core and accounts for valence-core interactions using MBPT. We apply this combined CI+MBPT method to calculate energy levels and transition amplitudes for Be, Mg, Ca, and Sr.

II. METHOD

A. Frozen-Core CI

We start with a lowest-order description of a divalent atom in which the closed N-2 electron core is described in the HF approximation and valence or excited electrons satisfy HF equations in the “frozen” V^{(N-2)} HF core. As we mentioned in the introduction, the strong valence-valence correlations must be included to infinite order; the CI method accomplishes this. The configuration space for divalent atoms is built up in terms of the single-particle basis orbitals i and j definite parity. We then expand the general two-particle wave function with angular momentum J and definite parity. We then expand the general twoparticle wave function Ψ_{JM} in terms of all Ψ_{JM}(ij) in our basis set

$$\Psi_{JM} = \sum_I c_I \Phi_I.$$  (1)

The expectation value of the Hamiltonian becomes

$$\langle \Psi_{JM} | H | \Psi_{JM} \rangle = \sum_I E_I c_I^2 + \sum_{I,K} V_{IK} c_I c_K,$$  (2)

where $E_I = e_i + e_j$ is the sum of single-particle HF energies and $V_{IK}$ is a first-order, two-particle correlation matrix element (see, for example, [21]) between the configurations $I = (ij)$ and $K = (kl)$. The variational condition leads to CI equations

$$\sum_K (E_I \delta_{IK} + V_{IK}) c_K = \lambda c_I,$$  (3)

from which CI energies ($\lambda$) and wave functions ($\sum_I c_I \Phi_I$) are found.

B. Combining CI with MBPT

Core polarization effects can be treated using MBPT. In this paper, we introduce two procedures that enable us to combine frozen-core CI and second-order two-valence-electron MBPT, which we refer to as “CI averaging” and “Brueckner-Orbital CI” methods.

1. CI averaging

In this first method, the core-valence interaction $\Delta E_{vc}$ is obtained by “averaging” MBPT corrections over CI wave functions:

$$\Delta E_{vc} = \sum c_I c_K \langle \Phi_I | H^{(2)} | \Phi_K \rangle,$$  (4)

where the configuration weights $c_I$ and $c_K$ are taken from the solution of the CI equation, Eq. (3), and $H^{(2)}$ is that part of the effective Hamiltonian projected onto the valence-electron subspace containing second-order valence-core interactions. The dominant second-order parts of the effective Hamiltonian, beyond those accounted for in the CI calculation, are the screening and self-energy diagrams: $H^{(2)} = H^{\text{screen}} + H^{\text{self}}$, the self-energy being much larger than the screening and both being larger than the remaining second-order terms.

We borrow ready-to-use formulas, derived using standard techniques, from Ref. [12]. The screening contribution to the effective Hamiltonian is

$$H^{\text{screen}}_{\nu'w'vw} = -\eta_{\nu'w'} \eta_{vw} \sum_{\alpha'\beta'\alpha\beta} C_{1}(\alpha'\beta'\alpha\beta) \times \sum_{n,k} \left( \begin{array}{ccc} j_{\nu'} & j_{\beta'} & J \\ j_{\alpha} & j_{\beta} & k \end{array} \right) \times \frac{Z_k(\alpha'bc)nZ_k(\beta'\eta\beta)}{\epsilon_\beta + \epsilon_{\beta'} - \epsilon_\alpha - \epsilon_n},$$  (5)

where

$$C_{1}(\alpha'\beta'\alpha\beta) = (-1)^I \left[ \delta_{\alpha\alpha'} \delta_{\beta\beta'} - \delta_{\alpha\beta'} \delta_{\alpha'\beta} + \delta_{\alpha\beta'} \delta_{\alpha'\beta} + \delta_{\alpha\alpha'} \delta_{\beta\beta'} \right]$$  (6)

The self-energy contribution to $H^{(2)}$ is

$$H^{\text{self}}_{\nu'w'vw} = \eta_{\nu'w'} \eta_{vw} \left[ \delta_{\nu'w'} \delta_{vw} + \delta_{\nu'w} \delta_{vw} \right] + (-1)^J \left[ \delta_{\nu'w'} \delta_{vw} + \delta_{\nu'w} \delta_{vw} \right],$$  (7)

where

$$\Sigma_{ij}(\epsilon_\alpha) = \sum_{kcmn} \frac{\eta_{\nu'w'} \eta_{vw}}{\left[ j_{i} \right] \left[ k \right]} \frac{X_k(icmn)Z_k(mn\eta c)}{\epsilon_\alpha + \epsilon_\epsilon - \epsilon_m - \epsilon_n} + \sum_{kbcn} \frac{\eta_{\nu'w'} \eta_{vw}}{\left[ j_{i} \right] \left[ k \right]} \frac{X_k(inbc)Z_k(bc\eta j)}{\epsilon_\alpha + \epsilon_\epsilon - \epsilon_b - \epsilon_c}.$$  (8)

In the above equations, J is the angular momentum of the coupled two-particle states. The coupled radial integrals $X_k(abcd)$ and $Z_k(abcd)$ are defined in [12]. We use
the notation $|k| = 2k + 1$. The quantities $\eta_{vw}$ are normalization constants, $\eta_{vw} = 1/\sqrt{2}$ for identical particle states and 1, otherwise. In the expression for the self-energy, the angular momenta of the $i$th and $j$th orbitals satisfy $\kappa_i = \kappa_j$, where $\kappa_i = \mp(j_i + 1/2)$ for $j_i = l_i \pm 1/2$ is the angular quantum number uniquely specifying the spion for state $i$. Since we found that the second-order self-energy correction is very important, we also consider the fourth-order self-energy obtained by iteration:

$$\Sigma_{ij}(\epsilon_0) \rightarrow \Sigma_{ij}(\epsilon_0) + \frac{\Sigma_{ik}(\epsilon_0) \Sigma_{kj}(\epsilon_0)}{\epsilon_i - \epsilon_k}. \tag{9}$$

In heavy atoms, the choice of $\epsilon_0$ deserves special consideration. Problems with denominators arise from the fact that single-particle orbitals used in the self-energy calculation are not optimal, in the sense that there is mutual interaction between valence electrons not accounted for, even approximately, in the $V^{(N-2)}$ potential and accounted for excessively in the $V^{(N)}$ potential which is used, for example, in Ref. 14. One practical solution to this problem is to use “optimized” denominators [14]. A consistent theory requires an ab-initio treatment of the denominator problem. Basing calculations of atoms with two valence electrons on a more realistic potential can reduce uncertainties in the choice of the denominator in the self-energy corrections.

We calculated energies of several levels using the CI averaging method and found that the best agreement with experiment for Be and Mg was obtained with $\epsilon_0$ equal to 1/2 of the CI energy. For the case of Ca, the best agreement was obtained choosing $\epsilon_0$ between 1/2 and 1 times the CI energy. One advantage of the CI averaging method is that the CI code is simple and that the CI wave functions can be stored and used many times. A cut-off condition can be imposed, as a compromise between speed and accuracy. The fastest approximation (giving the poorest accuracy) is obtained by restricting the MBPT corrections to the leading configurations. We used this leading configuration approximation to estimate the magnitude of the core-excitation effects as the first step in developing our computer code. Adjusting the cut-off condition, we readily reached a high level of accuracy (finally we chose the cut-off condition $|c_i c_k| < 0.002$ for all calculations). The energies for several states of Be, Mg, and Ca presented in this paper have been calculated with the CI averaging method. The principal drawback of this method is that wave functions necessary for calculations of other properties are not automatically obtained.

2. Brueckner-Orbital CI

The effective Hamiltonian formalism [12] leads to the problem of diagonalizing the Hamiltonian matrix built on the frozen-core two-electron configuration state functions $\Phi_I$. We split this matrix into functionally distinct pieces:

$$H = H^{(0)} + H^{(1)} + H^{(2)}, \tag{10}$$

where $H^{(0)}$ is the zeroth-order Dirac-Fock Hamiltonian, which in the Dirac-Hartree-Fock (DHF) basis is

$$H^{(0)}_{vw} = \delta_{vw} \delta_{ww'} (\epsilon_v^0 + \epsilon_w^0),$$

and $H^{(1)}$ is the first-order electron-electron interaction Hamiltonian

$$H^{(1)}_{v'w'vw} = V^{(1)}_{v'w'vw},$$

defined in Ref. 13. $H^{(2)}$ is the second-order correction which consists of the two-particle screening correction and the one-particle self-energy correction defined previously. In the CI averaging method, $H^{(0)} + H^{(1)}$ is diagonalized first in a DHF basis (where $H^{(0)}$ is diagonal) to give state energies and CI wave functions, then $H^{(2)}$ is evaluated using the CI wave functions to give corrections for the core-valence interaction.

In the Brueckner-orbital (BO) CI method, the basis functions are chosen as orthonormal solutions of the quasi-particle equation,

$$[\hbar^2 + V_{HF} + \Sigma_{ij}(\epsilon)] \phi_j = \epsilon^{BO} \phi_i. \tag{11}$$

In this BO basis,

$$\left( H^{(0)} + H^{\text{self}} \right)_{v'w'vw} = \delta_{vw} \delta_{ww'} (\epsilon_v^{BO} + \epsilon_w^{BO}). \tag{12}$$

The basis orbitals include second-order self-energy corrections together with the lowest-order DHF potential. The residual non-trivial part of the effective Hamiltonian in the BO basis is the sum $H^{(1)} + H^{\text{screen}}$. In the Bruckner orbital-CI method, the residual Hamiltonian matrix is evaluated in the BO basis and diagonalized to obtain state energies and CI wave functions. The BO-CI method is equivalent to CI averaging method if we neglect energy differences in the denominators of $H^{\text{self}}$ and $H^{\text{screen}}$ (of order of the valence-valence interaction energy), which are small compared to the core excitation energies. The BO-CI method is also equivalent to the effective Hamiltonian method in [14] to the same level of precision, provided all second-order diagrams are included. Some advantage is gained in accuracy compared to the CI averaging method, since the largest valence-core corrections [those from $\Sigma_{ij}(\epsilon_0)$] are taken into account to infinite order.

The Brueckner-orbital CI method is very convenient for calculations of transition amplitudes; once the residual interaction is diagonalized, the associated wave functions are immediately available. We include random-phase approximation (RPA) corrections in calculations of transition amplitudes by replacing “bare” matrix elements with “dressed” elements as explained in [20]. Length-form and velocity-form dipole matrix elements are found to be in close agreement in BO-CI calculations that include RPA corrections.
A comparison of the resulting CI energies with measured energies from the National Institute of Standards and Technology (NIST) database [22] is shown in Table I. This comparison provides the first test of the CI averaging method. The values listed in the table agree with experiment at the level of tens of cm\(^{-1}\). The residual deviation can be explained as neglect of small Coulomb and Breit diagrams, which will be the subject of future investigations.

It is also interesting to compare CI energies, with and without the MBPT corrections \(\Delta E_{cc}\), with energies from the NIST database. Such a comparison is given in Table II and illustrates the importance of the valence-core corrections.

The agreement with experiment improves by an order of magnitude for the CI-averaging method as compared with a frozen-core CI calculation. Indeed, we found it necessary to use the more precise energies obtained from the CI-averaging method to properly identify the transitions shown in this table.

### III. CALCULATIONS OF SPECTRA USING CI AVERAGING

The CI averaging method is fast and convenient for calculations of energies when a large number of levels are needed, especially at the stage of adjusting the code parameters. Below, we present our calculations for many levels of Be, Mg, and Ca atoms to demonstrate the accuracy of this method. We evaluate the valence-core correction \(\Delta E_{cc}\) to the CI energy using a subset of the CI coefficients limited to those satisfying \(|\epsilon_I \epsilon_K| \leq 0.002\). The parameter \(\epsilon_0\) in the self-energy was chosen to be \(\epsilon_{CI}/2\) for Be and Mg. For calcium it was increased to \(3\epsilon_{CI}/4\) to obtain better agreement for energies of the \(4p^2\) states.

The basis set used to set up the calculations consisted of 25/40 DHF basis functions for each value of \(l \leq 5\). The basis functions were formed as linear combinations of B-splines of order 7, constrained to a cavity of radius \(R=80 \ a_0\).

#### A. Calculations for Be

We chose to study a Be atom for several reasons. First, this atom has a small core and, consequently, requires relatively little computation time. Second, because of the small size of the core-valence interaction, calculations for Be are expected to be very precise.

| Config. | Term | J | NIST | CI-average | Diff. Frozen CI | Diff. |
|---------|------|---|------|-------------|----------------|-------|
| 2s\(^2\) | 1S  | 0 | 52081 | 52074       | 0              | -17   |
| 2s2p    | 3P\(^o\) | 0 | 21978 | 21996       | 0              | -18   |
| 2s2p    | 3P\(^o\) | 2 | 21981 | 22000       | 0              | -19   |
| 2s3s    | 3S  | 1 | 52081 | 52074       | 0              | -17   |
| 2p\(^2\) | 1D  | 2 | 56882 | 56890       | 0              | -8    |
| 2s3p    | 3P\(^o\) | 1 | 58907 | 58890       | 0              | -17   |
| 2s3p    | 3P\(^o\) | 2 | 58908 | 58896       | 0              | -16   |
| 2p\(^2\) | 3P  | 1 | 59695 | 59749       | 0              | -52   |
| 2p\(^2\) | 3P  | 2 | 59697 | 59747       | 0              | -50   |
| 2s3d    | 3D  | 3 | 62054 | 62033       | 0              | -21   |
| 2s3d    | 1D  | 2 | 64428 | 64414       | 0              | -14   |
| 2s4s    | 3S  | 1 | 64506 | 64528       | 0              | -22   |
| 2s4s    | 1S  | 0 | 65245 | 65261       | 0              | -16   |
| 2s4p    | 3P\(^o\) | 2 | 66812 | 66792       | 0              | -20   |
| 2s4d    | 3D  | 3 | 67942 | 67924       | 0              | -18   |
| 2s4f    | 3F\(^o\) | 3 | 68241 | 68224       | 0              | -17   |
| 2s4f    | 1F\(^o\) | 3 | 68241 | 68224       | 0              | -17   |
| 2s4d    | 1D  | 2 | 68781 | 68774       | 0              | -7    |
| 2s5s    | 3S  | 1 | 69010 | 69056       | 0              | -46   |

#### B. Calculations for Mg

Another example where the CI averaging method predicts energy levels accurately is magnesium. In this atom, however, core correlations are larger and the treatment of the valence-core interaction term requires more careful analysis. One important aspect is choosing the parameter \(\epsilon_0\) in the denominators of the MBPT corrections, another is the treatment of self-energy diagrams. We found mild sensitivity of final energies in Mg to the choice of \(\epsilon_0\). The corrected energies shown in the column headed ‘CI + 2nd’ in Table II, which were obtained with the choice \(\epsilon_0 = \epsilon_{CI}/2\), are seen to be in close agreement with experimental energies [22].

Typically, the self-energy correction is much larger than other valence-core diagrams; for example, in the Mg ground state, the self-energy is \(-1.65 \times 10^{-2}\) a.u. while the screening contribution is ten times smaller, \(1.83 \times 10^{-3}\) a.u. Valence-core contributions in fourth-order, obtained by iterating (or chaining) the second-order Brueckner corrections are also found to be significant, \(-6.57 \times 10^{-4}\) a.u. for the Mg ground state. The effect of including corrections from chaining the self-energy shown in the column headed ‘CI + 4th’ in Table II is seen to further improve the agreement with experiment.
is solved, various properties of atoms can be calculated theoretical eigenvalues. Once the question of classification a particular symmetry is the same as the sequence of the-

energy levels, more accurate CI+MBPT energies permit
accurately of frozen CI energies prevents the identification of
lower than for the lighter atoms. While the poor accu-
result, the final accuracy of CI+MBPT method is also
much stronger than in the case of Be and Mg. As a
the importance of the valence-core interaction, which is

TABLE III: Comparison of energies (a.u.) in Mg obtained from frozen-core CI, CI-averaging with 2nd-order self-energy, and CI-averaging with chained 4th-order self-energy, with experimental energies from the NIST database [22].

| Conf. Level | CI | CI+2nd | CI+4th | Expt. | Δ (cm$^{-1}$) |
|-------------|----|--------|--------|-------|--------------|
| $3s^2$ $^1S_0$ | 0.818 | 0.8329 | 0.833513 | 0.833518 | 1 |
| $3s4s$ $^1S_0$ | 0.624 | 0.6349 | 0.635260 | 0.635303 | 9 |
| $3s5s$ $^1S_0$ | 0.583 | 0.5938 | 0.594240 | 0.594056 | 40 |
| $3s6s$ $^1S_0$ | 0.566 | 0.5772 | 0.577813 | 0.577513 | 66 |
| $3p^2$ $^3P_0$ | 0.562 | 0.5605 | 0.569747 | 0.570105 | 79 |
| $3s3p$ $^3P_1$ | 0.723 | 0.7336 | 0.733991 | 0.733869 | 27 |
| $3s3p$ $^3P_1$ | 0.661 | 0.6733 | 0.673673 | 0.673813 | 31 |
| $3s4p$ $^3P_1$ | 0.604 | 0.6156 | 0.615834 | 0.615524 | 68 |
| $3s4p$ $^3P_1$ | 0.597 | 0.6086 | 0.608606 | 0.608679 | 16 |
| $3s3p$ $^3P_2$ | 0.723 | 0.7333 | 0.733867 | 0.733684 | 67 |

C. Ca atom

In Table IV, several even parity $J = 0$ levels are calculated with the frozen-core CI and CI-averaging methods. Compared to the frozen-core CI method, the agreement is significantly improved with the addition of MBPT corrections, changing the difference between experiment and theory from approximately one thousand cm$^{-1}$ to a few hundred cm$^{-1}$. This significant change clearly indicates the importance of the valence-core interaction, which is much stronger than in the case of Be and Mg. As a result, the final accuracy of CI-MBPT method is also lower than for the lighter atoms. While the poor accuracy of frozen CI energies prevents the identification of energy levels, more accurate CI+MBPT energies permit one to identify many Ca levels. It is interesting to notice that the sequence of experimental levels for the states of a particular symmetry is the same as the sequence of theoretical eigenvalues. Once the question of classification is solved, various properties of atoms can be calculated using, for example, frozen-core CI.

In the case of Ca, another problem that needs attention is the choice of the parameter $\epsilon_0$ in the self-energy, the dominant part of the core-valence interaction. We find that there is an optimal value of this parameter between $\epsilon_{CI}/2$, our standard value for Be and Mg, and $\epsilon_{CI}$, for which the ground state becomes very accurate. In Table V we chose this parameter to be 0.75 $\epsilon_{CI}$. In the following section, we will illustrate our calculations of transition amplitudes for several levels of Mg, Ca, and Sr where other precise calculations and measurements exist.

IV. CALCULATIONS USING THE BRUECKNER-ORBITAL CI METHOD

In this section, we present our calculations of energies and transition amplitudes with the Brueckner-orbital CI method. Our basis consisted of 25 $V_{HF}^{K-2}$ orbitals (those orbitals were constructed of 40 B-splines in the cavity 80 a.u.), in which 14 lowest excited states were replaced with Brueckner orbitals. The resulting one-valence electron energies for the divalent atoms were tested by comparing with experimental energies for the corresponding monovalent ions. For Mg$^+$, the BO energies agree with experiment better than do the second-order energies (Table V). A second iteration of the BO equation was also included in the CI-averaging method (Table III) to improve accuracy. The small size of the residual deviation from experiment in both tables can be attributed to higher-order diagrams. Two-particle screening corrections with the restriction $n < 15$ were included in the effective Hamiltonian, diagonalization of which provided the initial and final state wave functions necessary for the calculation of transition amplitudes. We checked that restrictions on the number of BO and screening diagrams included in the calculation did not lead to significant errors. Dressed transition amplitudes were used to take into account RPA corrections, which provide better length- and velocity-form agreement. We completely neglected the extremely time consuming structural radiation corrections which are expected to be small for the length form; for this reason, the result calculated

| States | DHF | 2nd order | BO | Expt. |
|--------|-----|-----------|----|------|
| $3s_{1/2}$ | 118825 | 121127 | 121184 | 121268 |
| $4s_{1/2}$ | 50588 | 51439 | 51446 | 51463 |
| $5s_{1/2}$ | 28233 | 28467 | 28469 | 28477 |
| $3p_{1/2}$ | 84295 | 85508 | 85542 | 85598 |
| $4p_{1/2}$ | 40250 | 40625 | 40633 | 40648 |
| $5p_{1/2}$ | 23642 | 23808 | 23811 | 23812 |

TABLE IV: Comparison of the accuracy of frozen-core CI and CI-averaging calculations for Ca. The parameter $\epsilon_0 = 0.75 \epsilon_{CI}$.

| Conf. Level | frozen CI | Diff. | CI-average | Diff. | Expt. |
|-------------|-----------|-------|------------|-------|------|
| $4s5s$ $^1S_0$ | 31901 | -1416 | 33196 | -121 | 33317 |
| $4p^2$ $^3P_0$ | 36699 | -1718 | 38900 | 483 | 38481 |
| $4s6s$ $^1S_0$ | 39376 | -1314 | 40504 | -186 | 40690 |
| $4p^2$ $^1S_0$ | 41480 | -306 | 42366 | 580 | 41786 |
| $4s7s$ $^1S_0$ | 42673 | -1604 | 43841 | -436 | 44277 |
| $4s8s$ $^1S_0$ | 44277 | -1610 | 45551 | -336 | 45887 |
| $4s9s$ $^1S_0$ | 45629 | -1206 | 46912 | 77 | 46835 |
TABLE VI: Comparison of the present transition energies $\omega$ (a.u.) and oscillator strengths $f$ for Be with those from other theories and experiment. A few allowed singlet–singlet transitions of the type $S_0^1 - P_1^1$ between low-lying states are considered. The experimental uncertainties are given in parentheses.

| Transition | Source  | $\omega$(Theory) | $\omega$(Expt.) | $f$  |
|------------|---------|------------------|-----------------|------|
| 2s$^2$-2s2p | present | 0.194126         | 0.193954        | 1.3750 | 1.38(0.12) |
|            |         | 0.91412          | 1.375           |
|            |         | 0.193914         | 1.374           |
|            |         | 1.3847           | 1.470           |
|            |         | 1.375            |                 |
| 2s$^2$-2s3p | present | 0.274231         | 0.274251        | 0.00904 |
|            |         | 0.27441          | 0.00901         |
|            |         | 0.274236         | 0.00914         |
|            |         | 0.0104           | 0.037           |
|            |         | 0.00885          |                 |
| 2s3s-2s2p  | present | 0.054977         | 0.05519         | 0.1188 |
|            |         | 0.05509          | 0.118           |
|            |         | 0.055198         | 0.1175          |
|            |         | 0.1199           | 0.140           |
| 2s3s-2s3p  | present | 0.025128         | 0.025107        | 0.9557 |
|            |         | 0.0252           | 0.958           |
|            |         | 0.025124         | 0.9656          |
|            |         |                 | 0.9615          |

in length form should be considered as more accurate. Small normalization corrections are also omitted.

A. Be case

The most accurate results for divalent atoms are expected for Be since it contains the smallest MBPT corrections. In Table VI, we compare our calculations with available precise calculations and experiment. Transition energies agree with experiment to better than 0.1%, except for the transition 2s3s$^1S - 2s2p^1P$ which has 0.4% accuracy. Our oscillator strengths agree well with those obtained in very accurate ab-initio calculations of Ref. [23] and in semiempirical calculations of Ref. [1] that reproduce energies very closely: for the principal transition 2s$^21S - 2s2p^1P$, our value 1.375 differs by 1 in the 4th digit from the value 1.374 in Ref. [23], the accuracy being better than 0.1%, and coincides with the value of Ref. [1]. Very close agreement with ab-initio theory is also achieved for the transition 2s3s$^1S - 2s3p^1P$. For suppressed transitions, an accuracy of 1% is obtained. Conducting a simple statistical analysis, we found that

TABLE VII: Comparison of BO-CI energies (cm$^{-1}$) with experiment for Mg, Ca, and Sr.

| Levels | Theory | Expt. | Diff. |
|--------|--------|-------|-------|
| Mg atom |        |       |       |
| 3s4s $^1S_0$ | 43452 | 43503 | 51    |
| 3s5s $^1S_0$ | 52517 | 52556 | 39    |
| 3s6s $^1S_0$ | 56154 | 56187 | 33    |
| 3s3p $^3P_1$ | 21834 | 21870 | 36    |
| 3s4p $^3P_1$ | 35059 | 35051 | 8     |
| 3s4p $^3P_1$ | 47806 | 47844 | 38    |
| Ca atom |        |       |       |
| 4s5s $^1S_0$ | 33505 | 33317 | 188   |
| 4p$^2$ $^3P_0$ | 38651 | 38418 | 233   |
| 4s6s $^1S_0$ | 40862 | 40690 | 172   |
| 4s4p $^3P_1$ | 15595 | 15210 | 385   |
| 4s4p $^3P_1$ | 23797 | 23652 | 145   |
| 4s5p $^3P_1$ | 36760 | 36555 | 205   |
| 4s5p $^3P_1$ | 36917 | 36732 | 185   |
| Sr atom |        |       |       |
| 5s6s $^1S_0$ | 30874 | 30592 | 282   |
| 5p$^2$ $^3P_0$ | 35913 | 35193 | 720   |
| 5p$^2$ $^3P_0$ | 37696 | 37160 | 536   |
| 5s5p $^3P_1$ | 15081 | 14504 | 577   |
| 5s5p $^3P_1$ | 21981 | 21699 | 282   |
| 5s6p $^3P_1$ | 34293 | 33868 | 425   |
| 5s6p $^3P_1$ | 34512 | 34098 | 414   |

energy differences in the CI-averaging and BO-CI calculations have similar statistical errors, but slightly different systematic shifts which can be explained partially by different denominators in the two methods. Another reason is the cut-off condition 0.002 in the former method and restriction on the number of Brueckner orbitals in the latter. The effect of the partial wave restriction on the ground state energy in both methods is 6 cm$^{-1}$. If this value is accounted for, the agreement becomes slightly better. The results in our tables are not extrapolated owing to the smallness of the omitted partial wave contributions.

B. The cases of Mg, Ca, and Sr

The accuracy of both the CI-averaging and the BO-CI calculations considered above decreases from light to heavy divalent atoms. Table VII illustrates this tendency in BO-CI calculations: for Mg, the theory-experiment differences range within 50 cm$^{-1}$, similar to what we have in Table VI, and for Ca the deviation from experiment increases to about 200 cm$^{-1}$ which is comparable to that in Table IV. The lowest accuracy is for Sr, which has the largest core and MBPT corrections. Similar re-
sults for energies have been obtained in Ref.\textsuperscript{14}. Our experiment-theory differences exhibit a systematic shift, which if subtracted, brings results into better agreement. For example, in Ca this shift is 216 cm\textsuperscript{-1}. After its subtraction, the residual deviation is 73 cm\textsuperscript{-1}. This subtraction procedure can be used in cases where closely spaced levels are difficult to identify. The systematic shift can be attributed to omitted correlations that affect mostly the ground state which is used as a reference. The cut-off condition in the CI-averaging method and restrictions on the number of BO and screening diagrams also has some effect on the accuracy of our results. This is one reason why the two methods give slightly different energies. In future development of our computer code, we will try to remove such restrictions completely. Another reason why the two methods give different results is that the choices of \( \epsilon_0 \) were different. In Table \textsuperscript{VIII} we illustrate our calculations of transition amplitudes for Mg, Ca, Sr. All of our transition amplitudes completely agree with those of recent CI+MBPT calculations by Porsev et al.\textsuperscript{14}, and are close to experimental values. Length-form and velocity-form amplitudes agree to better than 1\% for allowed transitions. Forbidden transitions are more problematic, owing to cancellation effects, and have poorer agreement between gauges and with experiment. The inclusion of the Breit interaction and negative-energy contributions, which are more important for the velocity form, might improve the situation. We also noticed that, if the balance between states such as \( p_{3/2} \) and \( p_{1/2} \) in relativistic basis is not properly maintained, the results for nonrelativistically forbidden transitions will be unstable. In addition, those transitions were affected by the number of BO and screening diagrams included in calculations. To minimize or exclude those effects in the BO-CI method, the BO orbitals and cut-off conditions were made completely symmetric with respect to \( l + 1/2 \) and \( l - 1/2 \) orbitals and included BO and screening corrections with number of excited orbitals less than 15.

V. SUMMARY AND CONCLUSION

In this paper, we have introduced two methods to improve the accuracy of the frozen-core CI calculations using MBPT: the CI-averaging method and the Brueckner-orbital CI method. We have applied these methods to Be, Mg, Ca, and Sr atoms. Our calculated energies and transition amplitudes for those atoms are in close agreement with the results of the best available theories and experiments. Compared to semiempirical theories, our method has an advantage in accuracy, and compared to other \textit{ab-initio} theories, an advantage of simplicity. These two methods can also be used to evaluate properties of Rydberg states for which only semiempirical calculations exist. Further improvement in accuracy is possible and is being pursued. This theory can be extended easily to treat particle-hole excited states of closed-shell atoms, atoms with three valence electrons, and other more complicated systems.

Acknowledgments

The authors are grateful to U. I. Safronova for helping to establish the correctness of computer codes. We are thankful to M. Kozlov for discussion of the theory. We thank H. G. Berry for reading manuscript and giving useful comments. We thank A. Derevianko for pointing out about experimental interest in divalent atoms. This work was supported in part by National Science Foundation Grant No. PHY-99-70666.

\[ \begin{aligned}
\text{Table VIII: Comparison of our length-form (L) and velocity-form (V) calculations with those from Ref.\textsuperscript{14} and with experiment.}
\end{aligned} \]

| \( ^1P_1(nsnp) - ^1S_0(ns^2) \) | Mg | Ca | Sr |
|----------------|----|----|----|
| L | 4.026 | 4.892 | 5.238 |
| V | 4.019 | 4.851 | 5.212 |
| Other\textsuperscript{a} | 4.03(2) | 4.91(7) | 5.28(9) |
| Expt. | 4.15(10)\textsuperscript{b} | 4.967(9)\textsuperscript{c} | 5.57(6)\textsuperscript{f} |
| Other\textsuperscript{a} | 4.06(10)\textsuperscript{e} | 4.99(4)\textsuperscript{d} | 5.40(8)\textsuperscript{h} |
| 4.12(6)\textsuperscript{d} | 4.93(11)\textsuperscript{g} | |
| \( ^3P_0(nsnp) - ^1S_0(ns^2) \) | L | 0.0063 | 0.0323 | 0.164 |
| V | 0.0070 | 0.0334 | 0.166 |
| Expt. | 0.0053(3)\textsuperscript{f} | 0.0357(4)\textsuperscript{d} | 0.1555(16)\textsuperscript{o} |
| Other\textsuperscript{a} | 0.0056(4)\textsuperscript{i} | 0.0352(10)\textsuperscript{m} | 0.1510(18)\textsuperscript{m} |
| 0.0061(10)\textsuperscript{h} | 0.0357(16)\textsuperscript{n} | 0.1486(17)\textsuperscript{p} |

\textsuperscript{a}Porsev et al.\textsuperscript{14}, \textsuperscript{b}Liljeby et al.\textsuperscript{14}, \textsuperscript{c}Landin et al.\textsuperscript{14}, \textsuperscript{d}Smith and Gallagher\textsuperscript{31}, \textsuperscript{e}Zinner et al.\textsuperscript{14}, \textsuperscript{f}Kelly and Mathur\textsuperscript{32}, \textsuperscript{g}Hansen\textsuperscript{33}, \textsuperscript{h}Parkinson et al.\textsuperscript{34}, \textsuperscript{i}Godone and Novero\textsuperscript{35}, \textsuperscript{j}Kwong et al.\textsuperscript{31}, \textsuperscript{k}Mitchell\textsuperscript{37}, \textsuperscript{l}Drozdowski et al.\textsuperscript{39}, \textsuperscript{m}Husain and Roberts\textsuperscript{38}, \textsuperscript{n}Husain and Schifino\textsuperscript{34}, \textsuperscript{o}Kelly et al.\textsuperscript{41}.

[1] M.-K. Chen, J. Phys. B \textbf{31}, 4523 (1998).  
[2] J. Mitroy, J. Phys. B \textbf{26}, 3703 (1993).
[3] C. J. Dai, Phys. Rev. A 52, 4416 (1995).
[4] M. H. Chen and K. T. Cheng, Phys. Rev. A 55, 166 (1997).
[5] M. H. Chen, K. T. Cheng, and W. R. Johnson, Phys. Rev. A 64, 042507 (2001).
[6] M. H. Chen and K. T. Cheng, Phys. Rev. A 55, 3440 (1997).
[7] C. F. Fischer, M. Godefroid, and J. Olsen, J. Phys. B 30, 1163 (1997).
[8] M. H. Chen and K. T. Cheng, Phys. Rev. A 55, 3440 (1997).
[9] M. H. Chen, K. T. Cheng, and W. R. Johnson, Phys. Rev. A 64, 042507 (2001).
[10] W. R. Johnson, M. S. Safronova, and U. I. Safronova, Physica Scripta 56, 252 (1997).
[11] M. S. Safronova, W. R. Johnson, and U. Safronova, Phys. Rev. A 53, 4036 (1996).
[12] St. F. Fischer, M. Godefroid, and J. Olsen, J. Phys. B 30, 1163 (1997).
[13] N. Vaeck, M. Godefroid, and J. E. Hansen, J. Phys. B 26, 361 (1991).
[14] P. Jonsson and C. F. Fischer, J. Phys. B 30, 5861 (1997).
[15] T. Brage and C. F. Fischer, Physica Scripta 48, 533 (1993).
[16] W. R. Johnson, M. S. Safronova, and U. I. Safronova, Physica Scripta 56, 252 (1997).
[17] Available at http://physics.nist.gov/cgi-bin/AtData.
[18] K. T. Chung and X.-W. Zhu, Phys. Rev. A 48, 1944 (1993).
[19] S. Hontzeas, I. Martinson, P. Erman, and R. Buchta, Physica Scripta 6, 55 (1972).
[20] I. Martinson, A. Gaupp, and L. J. Curtis, J. Phys. B 7, L463 (1974).
[21] R. Moccia and P. Spizzo, J. Phys. B 18, 3537 (1985).
[22] E. Markiewicz, R. P. McEachran, and M. Cohen, Physica Scripta 23, 828 (1981).
[23] J. Fleming, M. R. Godefroid, K. L. Bell, A. Hiebert, N. Vaeck, J. Olsen, P. Jonsson, and C. F. Fischer, J. Phys. B 29, 4347 (1996).
[24] L. Liljeb, A. Lindgard, and S. M. et al, Physica Scripta 21, 805 (1980).
[25] L. Lundin, B. Engman, J. Hilke, and I. Martinson, Physica Scripta 8, 274 (1973).
[26] W. W. Smith and A. Gallagher, Phys. Rev. A 145, 26 (1966).
[27] F. M. Kelly and M. S. Mathur, Can. J. Phys. 58, 1416 (1980).
[28] W. Hansen, J. Phys. B 16, 2309 (1983).
[29] W. H. Parkinson, E. M. Reeves, and F. S. Tomkins, J. Phys. B 9, 157 (1976).
[30] A. Godone and C. Novero, Phys. Rev. A 45, 1717 (1992).
[31] H. S. Kwong, P. L. Smith, and W. H. Parkinson, Phys. Rev. A 25, 2629 (1982).
[32] J. Mitchell, J. Phys. B 8, 25 (1975).
[33] D. Hussain and G. J. Roberts, J. Chem. Soc. Faraday Trans. 2 82, 1921 (1986).
[34] R. Drozdowski, M. Ignasiuk, J. Kwela, and J. Heldt, Z. Phys. D 41, 125 (1997).
[35] P. G. Whitkop and J. R. Wiesenfeld, Chem. Phys. Lett. 69, 457 (1980).
[36] D. Hussain and J. Schifino, J. Chem. Soc. Faraday Trans. 2 80, 321 (1984).
[37] J. F. Kelly, M. Harris, and A. Gallagher, Phys. Rev. A 37, 2354 (1988).