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Configuration-interaction many-body-perturbation-theory energy levels of four-valent Si I

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The mixed configuration-interaction (CI) many-body-perturbation-theory method is accurate in divalent atoms. In more complex atoms, with the number of valence electrons it becomes progressively more difficult to saturate CI space. Here, a four-valence electron atom, Si I, is considered. It is found that by using a relatively small cavity of 30 a.u. and by choosing carefully configuration space, it is possible to obtain quite accurate agreement between the theory and experiment. After subtraction of systematic shifts of 481 and −426 cm^{-1} for the lowest even and odd states, respectively, the deviation between theory and experiment becomes at the level of 100 cm^{-1}. This agreement is comparable to that in divalent atoms where the CI saturation has been achieved. It is anticipated that the approach can also give good results for atoms with more valence electrons to be considered in the future.

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I. INTRODUCTION

The spectra of complex atoms are of great interest in many applications. Neutral silicon, Si I, in particular has astrophysical importance due to its high abundance and significant contribution to solar and stellar opacities. Si atom properties are also needed for various industrial applications, including in nanotechnology. Several methods are available for accurate calculations of low states of Si I and other multivalence atoms that are based on multiconfiguration expansions. In the configuration-interaction (CI) method, the atomic states are expanded in the basis of fixed radial orbitals. While the method can be quite accurate for few-electron atoms, it has difficulty in atoms such as silicon due to a large size of full CI space. If CI is limited to the valence electron sector, the important core-excitation effects are neglected, but even the partial inclusion of configurations to account for these effects at reasonable level would lead to very large CI matrices. Double excitations, in particular, create two holes and two extra virtual electrons, so the number of particles in CI grows from 4 to 8. The configuration space can be decreased with multiconfiguration Hartree-Fock method (MCHF), in which the radial orbitals are optimized to approach the physical radial basis. Thus, fewer orbitals are required. Still, there are difficulties with including core excitations, and convergence of MCHF can be a problem. Another possibility is to use adjustable parameters to take into account core excitations, valence-valence interactions, and relativistic effects. This approach is implemented in Cowan's code [1]. The advantage of Cowan's code is that the energy can be fitted accurately to experimental values providing means of identification in complex spectra; however, wave functions are not necessarily accurate, as in other semiempirical methods. A most efficient *ab initio* way to include valence-core interactions is to combine CI and many-body perturbation theory (MBPT). Because valence-core interaction is relatively weak, MBPT can treat it with adequate accuracy, while CI can be constructed only from valence electrons.

Returning to Si I, its energies and transition properties have been computed with the relativistic Cowan code (relativistic MCHF with adjustable electrostatic parameters) [2], MCHF (the Breit-Pauli approximation) [3], B-spline *R*-matrix BSR code [4], and other methods. While in various methods, especially of semiempirical type, energy levels can be accurately reproduced, the lifetimes and transitions rates are not. A good comparison of experimental and theoretical lifetimes is provided in Ref. [5], which illustrates that Si I lifetimes obtained with the Cowan code have significant deviations from the experiment and more accurate theories.

In this paper, we use the CI-MBPT approach, which has not been applied to the Si I atom before. The CI-MBPT method is very accurate for divalent atoms, but for the majority of atoms with a larger number of valence electrons, the accuracy is lower due to difficulty of the saturation of the valence CI space. For example, if the basis is limited by the maximum principal number $N_{\max} = 8$ and angular momentum $l_{\max} = 3$, the number of CI states, as calculated with the CI-MBPT code, increases rapidly from Si III $J = 2$ to Si II $J = 3/2$ to Si I $J = 2$ for single (S), double (D), and triple (T) excitations from the ground state in the following progression: Si III: 12 → 352 → 352; Si II: 63 → 2077 → 11 912; Si I: 340 → 7007 → 86 582. Apparently for an atom with four valence electrons such as Si I to maintain a reasonable size of the CI matrix, either the triple excitations have to be restricted or the basis has to be substantially truncated compared to that typically used in divalent CI-MBPT calculations ($N_{\max} = 15$). Thus, some strategy is needed for both optimizing the basis and minimizing the number of states and configurations.

One approach that can help to substantially reduce the basis for expanding lowest states is to reduce the cavity size. The cavity is introduced into CI-MBPT calculations to replace the infinite number of Rydberg and continuum states with a small number of cavity-bound states. Because smaller cavities have larger spacing between the energy levels of the basis functions and because high-energy basis functions do not overlap much with low-energy atomic states of interest, for a given accuracy, $N_{\max}$ will be reduced. This approach is suitable as long as the calculated atomic wave functions and energy levels are not significantly perturbed by the cavity. Later, it will be shown that a cavity of 30 a.u. can be used to calculate a large number of lowest Si I states with a good accuracy. The second approach is to optimize the choice of configurations. Not all configurations couple strongly to the lowest states of interest, so by choosing an optimal set, a good level of accuracy might be possible to achieve with a reasonable number of configurations. In this regard, energy calculations for a four-valence electron ($4v$) atom such as Si I are of great interest to the theory as an intermediate step in calculations between currently well-understood divalent atoms and much more complex atoms such as Fe I, U I, etc., where even assignment of theoretical levels can be problematic due to the low accuracy of existing methods and possibility of order reversal between levels. Without unambiguous assignment, the theory cannot be reliably used for calculations of other, unknown properties. Moreover, in some cases energies might not be available altogether and alternative semiempirical methods cannot be used. Previously, calculations with the CI-MBPT method were performed for other $4v$ atoms such as Ge, Sn, Pb [6]. The comparison between results will be of interest to see the trend in accuracy. Si I has smallest relativistic and core-polarization corrections, which are treated quite accurately with the MBPT method, so the accuracy is mostly limited by the CI space saturation. The main focus of this work is on improving the accuracy of valence-valence CI part.

II. METHOD

In this work, a CI-MBPT method developed for open-shell atoms with multiple valence electrons is used (see for example [6]). The effective CI-MBPT Hamiltonian for Si I can be split into two parts:

$$H^{\mathrm{eff}} = \sum_{i=1}^{M} h_{1i} + \sum_{i\neq j}^{M} h_{2ij}. \tag{1}$$

The one-electron contribution

$$h_1 = c\alpha \cdot \mathbf{p} + (\beta - 1)mc^2 - Ze^2/r + V^{N-4} + \Sigma_1 \tag{2}$$

in addition to the V^{N-4} Dirac-Hartree-Fock (DHF) potential contains the valence electron self-energy correction Σ_1 [7]. In the current CI-MBPT program, the self-energy correction is calculated with the second-order MBPT. The two-electron Hamiltonian is

$$h_2 = e^2/|\mathbf{r_1} - \mathbf{r_2}| + \Sigma_2, \tag{3}$$

where Σ_2 is the term accounting for Coulomb interaction screening arising from the presence of the core [8]. In the program, the screening is also calculated in the second order. Further details on the CI-MBPT approach can be found in Ref. [9]. In terms of specific numerical steps, first, DHF V^{N-4} potential for the closed-shell Si V ion is calculated. Alternatively, Si III potential can be used, but additional subtraction diagrams will be required, which in some CI-MBPT codes are not incorporated. No significant improvement in accuracy of Si I energies has been observed by using the V^{N-2} potential. Second, the basis in the frozen V^{N-4} is calculated with the help of a B-spline subroutine for the ion in a cavity of radius R. The basis is then used to evaluate the CI-MBPT terms in Eq. (1). Finally, the eigenvalue problem is solved for the effective Hamiltonian matrix. The program generates a set of configurations by single, double, etc., excitations of the input configurations limited by the l_{max} and N_{max}.

III. CI-MBPT CALCULATIONS

To test the accuracy of CI-MBPT method in Si I, the energies of the lowest states with $J = 0 - 3$ that are not yet affected by the cavity shift have been calculated. This shift was estimated from trends in the deviations of energies from experiments for different cavity sizes, which starting with some energy for a given J and parity rapidly increases. The cavity shift for a given state is related to the removal energy of the least bound electron and its asymptotic behavior. In the final calculations, the cavity size of 30 a.u. has been adopted. The configurations were chosen as follows. For the even states $J = 0$–3, one and two electrons of the reference valence configurations $3s^2 3p^2$, $3s^2 3p4p$, and $3s4s3p^2$ were excited with the limits on the excited states $l_{\mathrm{max}} = 3$ and N_{max} that generated states with a specific J and parity. For example, single excitations from $3s^2 3p^2$ produce configurations of type $3sns3p^2$, $3snd3p^2$, $3s^2 3pnp$, and $3s^2 3pnf$, while double excitations produce configurations of type $3s^2 npmp$, $nsmp3p^2$, and many others. The number of double-excited states considerably exceeds the number of single-excited states. Some effective triplet excitations from the ground states are included via the initial choice of reference configurations. Similar procedure was carried out for the odd states. The reference configurations were chosen $3s3p^3$, $3s^2 3p4s$, and $3s^2 3p3d$. The list of nonrelativistic configuration was converted automatically to the list of relativistic configurations. The total number of states, the size of the effective Hamiltonian matrix, ranged from 6 to 30 k, depending on J and N_{max} as illustrated in Table I. Table I also illustrates that the deviation from experiment decreases for larger N_{max}, as expected. Unfortunately, currently the program has a limitation on the number of states about 34 k. To have uniform accuracy for the considered states with $J = 0$–3, we chose $N_{\mathrm{max}} = 8$ that resulted in the number of states not exceeding 34 k.

After various preliminary tests and optimizations of the cavities and configurations, as described above, we have calculated the energy levels for the lowest $J = 0$–3 states that are not affected by the cavity (30 a.u.). The even states are compiled in Table II. A close and consistent agreement has been achieved at the level of 400 cm^{-1}; however, it can be noted that a relatively constant systematic shift exists for all the considered levels, except for the fine-structure ground-state

TABLE I. Number of states (N_{states}) for given configuration input parameters. The basic configurations for the even states are $3s^2 3p^2$, $3s^2 3p4p$, and $3s4s3p^2$. The single and double excitations are restricted with $L_{\mathrm{max}} = 2$ and N_{max} specified in the table. Δ is the deviation of theoretical energies from experiment in cm^{-1}.

J	Parity	N_{max}	N_{states}	Δ
0	even	8	6073	569
0	even	10	11581	535
0	even	12	18857	459
0	even	14	27901	425
1	even	8	15847	327
2	even	8	20862	356
3	even	8	19999	389
0	odd	8	6806	– 482
0	odd	10	13062	– 408
0	odd	12	21342	– 332
0	odd	14	31646	– 130

TABLE II. Comparison of CI-MBPT and NIST (experimental) energy levels for the lowest $J = 0$–3 even states that do not have strong cavity perturbation. The differences between CI-MBPT and NIST energies have a substantial systematic shift $\overline{\Delta} = 481\,\mathrm{cm}^{-1}$, which if subtracted brings the theory in close agreement with experiment, at the level of 100 cm^{-1} (the last column). Such small residual deviation facilitates positive identification of the levels. The shift is not subtracted from the ground-state fine-structure levels. All energies are given in cm^{-1}.

Configurations	J	$E_{\mathrm{CI-MBPT}}$	E_{NIST}	Δ	$\Delta - \overline{\Delta}$
$3s^23p^2\ ^3\mathrm{P}$	0	0	0	0	0
$3s^23p^2\ ^1\mathrm{S}$	0	15963	15394	569	88
$3s^23p4p\ ^3\mathrm{P}$	0	49559	49028	531	50
$3s^23p4p\ ^1\mathrm{S}$	0	52325	51612	713	232
$3s^23\mathrm{p}^2\ ^3\mathrm{P}$	1	80	77	3	
$3\mathrm{s}^23p4p\ ^1\mathrm{P}$	1	47611	47284	327	− 154
$3s^23p4p\ ^3\mathrm{D}$	1	48398	48020	378	− 103
$3s^23p4p\ ^3\mathrm{P}$	1	49577	49061	516	35
$3s^23p4p\ ^3\mathrm{S}$	1	49843	49400	443	− 38
$3s^23p^2\ ^3\mathrm{P}$	2	234	223	10	
$3s^23p^2\ ^1\mathrm{D}$	2	6655	6299	356	− 125
$3s^23p4p\ ^3\mathrm{D}$	2	48485	48102	383	− 98
$3s^23p4p\ ^3\mathrm{P}$	2	49726	49189	537	56
$3s^23p4p\ ^1\mathrm{D}$	2	50823	50189	634	153
$3s^23p4p\ ^3\mathrm{D}$	3	48654	48264	389	− 92

levels (of the same configuration). The nature of the shift is not clear, but it can most likely be attributed to the omitted states $n > N_{\max}$, especially belonging to continuum. Actually, Table I shows that at least in the case of $J = 0$ with increase in $N_{\max}$ the shift is substantially reduced for both even and especially odd states. (Note that other J states of Si I and generally of other more complex atoms require the number of configurations beyond the current limit, so the trends with $N_{\max}$ are difficult to investigate.) This trend for $J = 0$ states and the fact that the shift is similar for other J states allow us to implement an *ab initio* shift removal by calculating it for lowest-J states ($J = 0$ in our specific case) in the limit of large $N_{\max}$. Alternatively, the shift can be removed semiempirically when some or all experimental levels are available. We chose the semiempirical approach to illustrate in Table II the ultimate reduction in deviation. After subtracting the average shift, found to be 481 cm^{-1}, the level of agreement with experiment becomes much better, at the level of 100 cm^{-1}. The shift subtraction, although it does not improve apparently wave functions, can help in the positive identification of levels.

Similar accuracy and the systematic shift are observed between CI-MBPT and NIST energies in odd states (Table III). However, the shift is negative, $-426\ \mathrm{cm}^{-1}$. If subtracted, it brings experiment and theory in agreement at the 100-cm^{-1} level. The increase in $N_{\max}$ from 8 to 14 for $J = 0$ states leads to the reduction of the deviation from -482 to $-130\ \mathrm{cm}^{-1}$, by 352 cm^{-1}, which is close to 452 cm^{-1}, the average systematic shift for all levels in Table III. For odd states, it seems possible to predict the shift *ab initio* with quite good accuracy using the lowest $J = 0$ state.

TABLE III. Comparison of CI-MBPT and NIST (experimental) energy levels for lowest $J = 0$–3 odd states. A systematic shift $\overline{\Delta} = -426\ \mathrm{cm}^{-1}$ if subtracted brings the theory in close agreement with experiment, at the level of 100 cm^{-1} (the last column). The ground-state fine-structure levels do not have large shift.

Config.	J	$E_{\mathrm{CI-MBPT}}$	E_{NIST}	Δ	$\Delta - \overline{\Delta}$
$3s^23p4s\ ^3\mathrm{P}$	0	39201	39683	−482	− 56
$3s^23p3d\ ^3\mathrm{P}$	0	50257	50602	−345	81
$3s^23p5s\ ^3\mathrm{P}$	0	53797	54245	−448	− 22
$3s^23p4d\ ^3\mathrm{P}$	0	56415	56733	−319	107
$3s^23p4s\ ^3\mathrm{P}$	1	39282	39760	−479	− 53
$3s^23p4s\ ^1\mathrm{P}$	1	40606	40992	−386	40
$3s3p^3\ ^3\mathrm{D}$	1	44852	45276	−424	2
$3s^23p3d\ ^3\mathrm{P}$	1	50219	50566	−347	79
$3s^23p3d\ ^1\mathrm{P}$	1	52957	53387	−430	− 4
$3s^23p3d\ ^3\mathrm{D}$	1	53725	54185	−460	− 34
$3s^23p5s\ ^3\mathrm{P}$	1	53869	54314	−445	− 19
$3s^23p5s\ ^1\mathrm{P}$	1	54460	54871	−411	15
$3s3p^3\ ^5\mathrm{S}$	2	32507	33326	−819	− 393
$3s^23p4s\ ^3\mathrm{P}$	2	39485	39955	−470	− 44
$3s3p^3\ ^3\mathrm{D}$	2	44871	45294	−422	4
$3s^23p3d\ ^1\mathrm{D}$	2	46944	47352	−408	18
$3s^23p3d\ ^3\mathrm{F}$	2	49559	49851	−292	134
$3s^23p3d\ ^3\mathrm{P}$	2	50149	50500	−351	75
$3s^23p3d\ ^3\mathrm{D}$	2	53745	54205	−460	− 34
$3s^23p5s\ ^3\mathrm{P}$	2	54093	54528	−435	− 9
$3s3p^3\ ^3\mathrm{D}$	3	44903	45322	−419	7
$3s^23p3d\ ^3\mathrm{F}$	3	49647	49934	−287	139
$3s^23p3d\ ^1\mathrm{F}$	3	52931	53362	−431	− 5
$3s^23p3d\ ^3\mathrm{D}$	3	53800	54258	−457	− 31

IV. DISCUSSION AND CONCLUSION

Atoms with four valence elections were not much investigated with the precision CI-MBPT method in the literature, with the notable exception being work by Dzuba [6] motivated by the alpha-variation project. Lead is of additional interest to theory due to parity-nonconservation (PNC) fundamental symmetry experiments [10–12].

On examples of $J = 0$–3 even and odd states we have shown that CI-MBPT theory gives good results if appropriate cavity and configurations are chosen, especially when systematic shifts are removed. This should be compared to calculations by Dzuba [6] for Ge, Sn, and Pb. In Ge I for the states beyond the ground-state fine-structure manifold, the deviation of theory from experiment on the order of 1000 cm^{-1} is observed. Moreover, although there are two different systematic shifts for even and odd states that can be removed to improve accuracy, the deviation still remains at 300 cm^{-1} for odd states. Even states reveal better accuracy, but the number of levels considered is quite small to evaluate the performance of theory by analyzing statistics. In Sn I the situation is similar; however, the MBPT core-valence corrections become larger, more than 1000 cm^{-1} and require more careful treatment. In Si I, the valence-core corrections are the smallest and omitted high-order effects are insignificant.

The deviation of energies from experiment of the MCHF method (the Breit-Pauli approximation) [3] ranges to

1000 cm^{-1}, although many states have quite small deviations below 100 cm^{-1}. No specific systematic shift can be identified. The lifetimes are in good agreement with experiment as well. At this point, it is not clear which method is better, but it is definitely important to have independent calculations to avoid a bias existing in each approach. It seems that even slightly better accuracy is achieved in B-spline R-matrix calculations [4], also based on expansions using MCHF calculations.

In this paper, we have demonstrated that CI-MBPT theory performs well for Si I and there are ways for improving accuracy. We have observed systematic shifts for even and odd systems of states, and if these shifts are subtracted the deviation of theory from experiment become at the level of 100 cm^{-1}. This is almost an order of magnitude improvement over CI-MBPT calculations in Sn I. The shifts can be attributed to the omitted high-energy states in CI, and in some cases the shifts can be predicted *ab initio* using the lowest states that require smallest number of configurations. In order to obtain energies for a relatively large number of states, we have chosen the cavity 30 a.u., a compromise between the cavity shift effect and the speed of convergence with the number of excited states. In addition to choosing carefully the cavity, the configurations also were chosen in such a way that the deviations of theory from experiment became quite uniform. Finally, we hope in the future the method can be further developed to treat most atoms in the periodic table as complex as actinides.

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