Configuration-interaction plus many-body-perturbation-theory calculations of Si I transition probabilities, oscillator strengths, and lifetimes

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(Received 22 December 2015; published 25 February 2016)

The precision of the mixed configuration-interaction plus many-body-perturbation-theory (CI+MBPT) method is limited in multivalence atoms by the large size of valence CI space. Previously, to study this problem, the CI+MBPT method was applied to calculations of energies in a four-valence electron atom, Si I. It was found that by using a relatively small cavity of 30 a.u. and by choosing carefully the configuration space, quite accurate agreement between theory and experiment at the level of 100 cm^{-1} can be obtained, especially after subtraction of systematic shifts for groups of states of the same J and parity. However, other properties are also important to investigate. In this work, the CI+MBPT method is applied to studies of transition probabilities, oscillator strengths, and lifetimes. A close agreement with accurate experimental measurements and other elaborate theories is obtained. The long-term goal is to extend the CI+MBPT approach to applications in more complex atoms, such as lantanides and actinides.

DOI: 10.1103/PhysRevA.93.022511

I. INTRODUCTION

Many applications require data on transition probabilities, lifetimes, and oscillator strengths of complex atoms. The Si I spectrum is of particular interest owing to its high abundance and significant contribution to solar and stellar opacities. The directly available experimental data are lifetimes [1–3] and branching ratios [3,4], from which transition probabilities and oscillator strengths were derived [3,4]. Precision calculations of transition probabilities and lifetimes were performed in [5] and weighted oscillator strengths in [6]. Semiempirical methods that can accurately reproduce energy levels do not necessarily lead to accurate lifetimes and transitions rates, as illustrated in Ref. [7] where the lifetimes obtained with the Cowan code [8] showed significant deviations from those obtained experimentally and with *ab initio* theories.

Previously, the CI+MBPT method, which can achieve high precision in multivalence atoms, was applied to calculations of energy levels for many low-lying levels of Si I and good agreement was observed [9]. In this work, the CI+MBPT method is applied to calculations of transition probabilities, lifetimes, and oscillator strengths. The optimization of the basis, the cavity radius, and the choice of configurations was done in a similar way as in [9]. A comparison with experiment and other theories will be given for transition probabilities, oscillator strengths, and lifetimes for which high-quality data are available [3].

One approach that helped to substantially reduce the basis for expanding lowest states was to reduce the cavity size, which 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, the maximum number N_{max} of radial functions required 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. It was shown that a cavity of 30 a.u. is suitable for calculations of a large number of energies of lowest Si I states [9]. It will be shown here that such a cavity is also suitable for matrix element calculations of many lowest Si I states.

In addition to Si I [9], energy calculations with the CI+MBPT method were performed for other $4v$ atoms such as C [10] and Ge, Sn, Pb [11]. However, CI+MBPT code was not used for systematic studies of transition probabilities in these atoms, Si in particular. This work fills the gap as well as will set the basis for studies of transition rates in more complex atoms.

II. METHOD

In this work a CI+MBPT method developed for open shell atoms with multiple valence electrons is used (see for example [11]). The optimization of configurations and the basis is the same as in [9]. Briefly, the theory can be summarized as follows. The effective CI+MBPT Hamiltonian for Si I is split into two parts:

$$H^{\rm eff} = \sum_{i=1}^{M} h_{1i} + \sum_{i\neq j}^{M} h_{2ij}. \qquad (1)$$

TABLE I. Comparison of the accuracy of CI+MBPT Si I energies (in cm^{-1}) for two cases: $l_{max} = 4$, current calculations, and $l_{max} = 3$, previous calculations [9]; Δ_4 and Δ_3 are deviations of theoretical energies from experiment for $l_{max} = 4$ and $l_{max} = 3$ cases, respectively.

State	Theor. $l_{max} = 4$	NIST	Δ_4	Δ_3
$J = 0$ even				
$3s^2 3p^2\ ^1S$	15871	15394	477	569
$3s^2 3p4p\ ^3P$	49593	49028	565	531
$3s^2 3p4p\ ^1S$	52355	51612	743	713
$J = 1$ odd				
$3s^2 3p4s\ ^3P$	39304	39760	−456	−479
$3s^2 3p4s\ ^1P$	40614	40992	−378	−386
$3s3p^3\ ^3D$	44840	45276	−436	−424
$3s^2 3p3d\ ^3P$	50185	50566	−381	−347

TABLE II. CI+MBPT Si I transition probabilities and comparison with precision experiment [3] and Breit-Pauli length-form [5] (LBP) calculations; Δ_1 and Δ_2 are deviations of CI+MBPT and LBP transition probabilities from the experiment; units are 10^6 s^{-1}; the same abbreviated term notations are used as in [3].

Odd	$3p^2$	λ (nm)	Expt.	CI+MBPT	Δ_1	LBP	Δ_2
$4s\ ^3P_0$	$^3P_1$	252.411	222 ± 11	228	6	229	7
$4s\ ^3P_1$	$^3P_0$	251.432	74.0 ± 3.8	75.6	1.6	76.5	2.5
	$^3P_1$	251.920	54.9 ± 2.9	56.4	1.5	57.0	2.1
	$^3P_2$	252.851	90.4 ± 4.6	94.3	3.9	94.9	4.5
	$^1D_2$	298.765	2.67 ± 0.25	2.06	−0.6		
	$^1S_0$	410.294	<0.44 ± 0.14	0.0988	−0.34		
$4s\ ^3P_2$	$^3P_1$	250.690	54.7 ± 2.8	57.6	2.9	58.4	3.7
	$^3P_2$	251.611	168 ± 8	172	4	174	6
	$^1D_2$	297.036	0.0600 ± 0.0084	0.040	−0.02		
$4s\ ^1P_1$	$^3P_0$	243.877	0.791 ± 0.061	0.773	−0.018		
	$^3P_1$	244.336	0.628 ± 0.057	0.607	−0.021		
	$^3P_2$	245.212	0.581 ± 0.059	0.548	−0.033		
	$^1D_2$	288.158	217 ± 11	242	25	237	20
	$^1S_0$	390.552	13.3 ± 0.7	14.6	1.3	13.1	−0.2
$3p^3\ ^3D_1$	$^3P_0$	220.798	26.2 ± 1.4	26.9	0.7	20.3	−5.9
	$^3P_1$	221.174	18.1 ± 1.0	19.3	1.2	14.8	−3.3
	$^3P_2$	221.892	1.05 ± 0.15	1.17	0.12	0.930	−0.12
	$^1D_2$	256.483		0.017			
	$^1S_0$	334.557		0.00092			
$3p^3\ ^3D_2$	$^3P_1$	221.089	34.5 ± 1.7	36.3	1.8	27.3	−7.2
	$^3P_2$	221.806	10.9 ± 0.6	11.0	0.1	8.57	−2.33
	$^1D_2$	256.368		0.0226			
$3p^3\ ^3D_3$	$^3P_2$	221.667	45.4 ± 2.3	47.1	1.7	35.7	−9.7
	$^1D_2$	256.182		0.00002			
$3d\ ^1D_2$	$^3P_2$	212.119	0.107 ± 0.015	0.119	0.012		
	$^1D_2$	243.515	44.3 ± 2.2	46.2	1.9	40.7	−3.6
$3d\ ^3P_2$	$^3P_1$	198.323	21.8 ± 1.1				
	$^3P_2$	198.899	65.7 ± 3.3	68.0	2.3	58.5	−7.2
	$^1D_2$	226.169	<0.175 ± 0.045	0.123	−0.05		
$3d\ ^3P_1$	$^3P_0$	197.760	27.9 ± 1.4	30.3	2.4	26.2	−1.7
	$^3P_1$	198.062	20.7 ± 1.1	21.9	1.2	19.3	−1.4
	$^3P_2$	198.636	36.5 ± 1.8	37.8	1.3		
$3d\ ^3P_0$	$^3P_1$	197.921	87.0 ± 4.3	89.3	2.3	77.6	−9.4
$3d\ ^1F_3$	$^3P_2$	188.185	5.00 ± 0.60	2.27	−2.73		
	$^1D_2$	212.412	298 ± 15	329	31	331	33
$3d\ ^1P_1$	$^3P_0$	187.310	1.65 ± 0.18				
	$^3P_1$	187.582	2.24 ± 0.26	2.11	−0.13		
	$^3P_2$	188.097	0.294 ± 0.029	0.350	0.056		
	$^1D_2$	212.299	7.1 ± 1.3	6.75	−0.35		
	$^1S_0$	263.128	106 ± 5				

The one-electron contribution

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

in addition to the V^{N-4} DHF potential contains the valence electron self-energy correction, Σ_1 [12]. In the current CI+MBPT program, the self-energy correction is calculated with the second-order MBPT. The two-electron Hamiltonian is

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

where Σ_2 is the term accounting for Coulomb interaction screening arising from the presence of the core [13]. In the program, the screening is also calculated in the second order. Further details on the CI+MBPT approach can be found in Ref. [14]. In terms of specific numerical steps, first, Dirac-Hartree-Fock (DHF) V^{N-4} potential for the closed-shell Si V ion is calculated. 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 a given maximum angular momentum $l_{\max} = 4$ and $N_{\max}$.

III. CI+MBPT CALCULATIONS

The accuracy of CI+MBPT method in Si I was tested on energies in [9]. We use here the same procedure for

TABLE III. Comparison of weighted oscillator strengths for Si I.

Lower level	Upper level	CI+MBPT	Theor. [6]	Theor. [5]	Expt. [3]
$3s^2 3p^2\ ^3P$	$3s^2 3p4s\ ^3P^\circ$	1.953	1.907	1.908	1.893 ± 0.098
	$3s^2 3p3d\ ^3P^\circ$	0.477	0.404	0.378	0.461 ± 0.024
	$3s3p^3\ ^3D^\circ$	0.521	0.471	0.394	0.501 ± 0.026
	$3s^2 3p3d\ ^3D^\circ$	1.978	1.885	2.165	
$3s^2 3p^2\ ^1D$	$3s^2 3p3d\ ^1F^\circ$	1.561	1.488	1.539	1.409 ± 0.073
	$3s^2 3p4s\ ^1P^\circ$	0.904	0.878	0.873	0.811 ± 0.042
	$3s^2 3p3d\ ^1D^\circ$	0.205	0.193	0.182	0.197 ± 0.010
	$3s^2 3p3d\ ^1P^\circ$	0.014	0.011	0.016	0.014 ± 0.001
$3s^2 3p^2\ ^1S$	$3s^2 3p4s\ ^1P^\circ$	0.100	0.103	0.097	0.091 ± 0.005
	$3s^2 3p3d\ ^1P^\circ$	0.348	0.323	0.345	0.330 ± 0.017

generating configurations and the same basis, the frozen Dirac-Hartree-Fock $V^{(N-4)}$, with the cavity size chosen 30 a.u. The program has been modified to allow a larger number of configurations. The configurations were chosen as follows. For the even states of different J, 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 $l_{\max} = 4$ and $N_{\max} = 8$ 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 increase of $l_{\max}$ from 3 (Ref. [9]) to 4 (current calculations) did not change energies much, Table I, so the quality of energies and wave functions is expected to be similar.

The transition properties are calculated using matrix element subroutines that also include the random-phase approximation (RPA) correction. The resulting transition probabilities are given in Table II. The expected accuracy for strong transitions, evaluated from the accuracy of transition energies, is on the order of 1 %–3 %; the accuracy of intercombination and accidentally weak transitions is lower and depends on the degree of cancellation and relativistic effects. The package has only length form output for the electric dipole transitions, so the difference between length and velocity forms cannot be used for testing the accuracy of the matrix elements. It can be seen that the current CI+MBPT transition probabilities are in complete agreement with experiment [3], except for some suppressed transitions, for which the theoretical accuracy decreases as expected. The comparison with experiment for suppressed transitions can serve as the estimate of theoretical accuracy when the experiment data are sufficiently accurate, and by generalization, the accuracy can be assumed the same for other similar weak transitions, on the order of 10 % for the data presented. The agreement of Breit-Pauli calculations [5] is also good, although in several cases the deviations exceed several error bars, indicating the theoretical error. In addition to transition probability, the weighted oscillator strengths are also given to include other accurate calculations [6] in comparison.

Finally, the comparison for lifetimes is shown in Table IV. The theoretical accuracy is expected similar to that of transition probabilities, a few percent. Again CI+MBPT agrees with precision measurements. Lifetimes have been measured by many groups, but it appears that the most reliable are measurements performed in Ref. [3].

IV. DISCUSSION AND CONCLUSION

Transition matrix elements of four-valence atoms were not previously calculated with the CI+MBPT method, and this work serves to fill the gap. The current method performed somewhat better than the Breit-Pauli method [5] for most experimentally available transition probabilities. For example, Breit-Pauli transition probabilities between $3p^3\ ^3D_1$ and $3p^2\ ^3P$ states deviate from experiment more than two standard deviations, while CI+MBPT values are in much better agreement. A good agreement of CI+MBPT for weighted oscillator strengths, initially listed in Ref. [6], is also achieved. The results of the other precision theories shown in Table III also agree with experiment. This comparison is useful to further verify the accuracy of the theory [6], which is used in electron scattering calculations. Finally, lifetime comparison is useful as well, since many measurements are available. The current theory agrees with most lifetime measurements, including those of [3] and [2] listed in Table IV. In addition to testing CI+MBPT theory, theoretical predictions for four weak intercombination transitions, which were not observed

TABLE IV. Si I lifetimes in ns of lowest odd levels.

Level	Energy (cm^{-1})	Present	Theor. [5]	Expt. [3]	Expt. [2]
$4s\ ^3P_0$	39683.16	4.39	4.374	4.5 ± 0.2	
$4s\ ^3P_1$	39760.29	4.38	4.352	4.5 ± 0.2	
$4s\ ^3P_2$	39955.05	4.36	4.307	4.5 ± 0.2	5.9 ± 0.7
$4s\ ^1P_1$	40991.88	3.87	3.969	4.3 ± 0.2	4.1 ± 0.2
$3p^3\ ^3D_1$	45276.19	21.1	27.80	22.0 ± 1.1	
$3p^3\ ^3D_2$	45293.63	21.2	27.89	22.0 ± 1.1	
$3p^3\ ^3D_3$	45321.85	21.2	28.03	22.0 ± 1.1	20.4 ± 1.0
$3d\ ^1D_2$	47351.55	21.6	24.54	22.5 ± 1.1	21.3 ± 1.0
$3d\ ^3P_1$	50566.40	11.1	12.83	11.7 ± 0.6	
$3d\ ^3P_0$	50602.44	11.2	12.75	11.5 ± 0.6	
$3d\ ^1F_3$	53362.24	2.99	2.984	3.3 ± 0.2	

experimentally, at 256.483, 335.557, 256.368, and 256.182 nm are also listed.

In conclusion, the CI+MBPT method was applied to calculations of electric-dipole matrix elements, and derived transition probabilities, oscillator strengths, and lifetimes are found in excellent agreement with experiment. This agreement supports high accuracy of both the experiment [3] and the CI+MBPT theory. In order to obtain energies for a relatively large number of states, the cavity was chosen 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 the cavity carefully, the configurations also were chosen in such a way that the deviations of theoretical energies from experiment became quite uniform. Finally, it is expected that in the future the method can be further developed to treat most complex atoms, including lantanides and actinides.

ACKNOWLEDGMENTS

The work of I.M.S. has been performed under the auspices of the U.S. DOE by LANL under Contract No. DE-AC52-06NA25396. The author is grateful to Dr. Dzuba for making his CI+MBPT code available for this work and many useful discussions.

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