Relativistic configuration-interaction study of transition probabilities in mercury with *ab initio* model potential wave functions

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The relativistic configuration-interaction method based on numerical Dirac-Fock wave functions (CIDF) is employed to determine $6s6p\ ^3P_{0,1,2}$, $^1P_1-6s7s\ ^3S_1,{}^1S_0$ transition energies and probabilities in mercury. The influence of electron correlation on both transition energies and probabilities is investigated. An alternative approach to the generation of spin orbitals used to construct configuration interaction wave functions is proposed. This is a configuration interaction method with relativistic wave functions generated using an *ab initio* model potential [CIDF(MP)]. The CIDF(MP) method is tested for resonance spin-forbidden and spin-allowed $6s^2\ ^1S_0-6s6p$ transitions in mercury and later successfully used for $6s6p-6s7s$ transition array.

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I. INTRODUCTION

In atomic structure calculations for heavy systems such as mercury two effects play decisive role. These are relativistic effects and electron correlation and since they are not additive they should be accounted for simultaneously. Both effects are taken into account in the relativistic multiconfiguration Dirac-Fock method (MCDF) which allows for simultaneous optimization of configuration-mixing coefficients and relativistic atomic orbitals. Despite the recent progress in development of MCDF method and its use for large-scale calculations we feel that the problem of computation of atomic transition probabilities or oscillator strengths (not energies), particularly for heavy many electron systems such as mercury, is still a difficult task in fully self-consistent MCDF approach. Therefore, the configuration-interaction method using numerical Dirac-Fock wave functions (CIDFs) combined with nonstandard techniques based on *ab initio* potential ideas in order to improve the efficiency of the CI procedure, may be worth consideration. In this paper we propose and test such approach for the $6s^2-6s6p$ and $6s6p-6s7s$ transition arrays.

II. CALCULATIONS

Relativistic Dirac-Fock calculations of the $6s6p-6s7s$ transition probabilities in HgI were performed using Desclaux's computer code [1] modified by us for the purpose of this study. To investigate the influence of electron correlation on the transition probabilities following calculations were carried out.

A. Single-manifold Dirac-Fock calculations

In the single-manifold Dirac-Fock calculations (SMDF) the lower and upper states were described by relativistic counterparts of dominating nonrelativistic configurations $6s6p$ and $6s7s$, respectively. The $6s6p\ ^3P_1$, $^1P_1$ states were described in the intermediate coupling

$$|6s6p\ ^3P_1\rangle = a_1|6s_{1/2}6p_{1/2}J=1\rangle + a_2|6s_{1/2}6p_{3/2}J=1\rangle,$$
(1)

$$|6s6p\ ^1P_1\rangle = b_1|6s_{1/2}6p_{1/2}J=1\rangle + b_2|6s_{1/2}6p_{3/2}J=1\rangle.$$
(2)

The other states were pure jj states:

$$|6s6p\ ^3P_0\rangle = |6s_{1/2}6p_{1/2}J=0\rangle,$$
(3)

$$|6s6p\ ^3P_2\rangle = |6s_{1/2}6p_{3/2}J=2\rangle,$$
(4)

$$|6s6p\ ^3S_1\rangle = |6s_{1/2}7s_{1/2}J=1\rangle,$$
(5)

$$|6s6p\ ^1S_0\rangle = |6s_{1/2}7s_{1/2}J=0\rangle.$$
(6)

All spin orbitals were determined in SCF process to minimize the energy of a given J state (optimal level scheme). For each of the states the convergence was achieved separately. The ''relaxed-core'' approximation was used throughout these calculations. In order to assess the influence of nonorthogonal $6s_{1/2}$ orbitals used in ''relaxed-core'' calculations, the additional computations were performed keeping the core and $6s$ orbital frozen in the $6s^2\ ^1S_0$ ground state. The obtained spin-forbidden $6s^2\ ^1S_0-6s6p\ ^3P_1$ transition oscillator strength is (up to the fourth decimal digit) the same as for fully relaxed calculations (0.01680). For the $6s6p-6s7s$ triplet-triplet transitions the difference is also very small, typically $4.17\times10^7\ \mathrm{s}^{-1}$ for $6s6p\ ^3P_1-6s7s\ ^3S_1$ transition probability vs $4.63\times10^7\ \mathrm{s}^{-1}$ for fully relaxed calculations. Larger differences (up to 40%) can be found for $6s6p-6s7s$ transitions with $\Delta S\neq0$, however, even here they cannot be responsible for discrepancies with experimental data which are of one order of magnitude.

B. Configuration-interaction Dirac-Fock calculations (CIDF)

In these calculations intravalence as well as core-valence electron correlation were taken into account through mixing of relativistic configurations. To include intravalence electron correlation the basis set comprised of the $\{1s^2\cdots5d^{10}\}n_1l_1j_1n_2l_2j_2$ configurations (with all valence nlj spin orbitals up to $9p$ except for nf spin orbitals with $n\geq6$). The core-valence electron correlation was represented by $\{1s^2\cdots5d^9\}n_1l_1j_1n_2l_2j_2n_3l_3j_3$ configurations

TABLE I. The $6s6p-6s7s$ transition array energies (in a.u.) in HgI (for a description of theoretical methods see text).

Transition	SMDF	CIDF	CIDF(MP)	Experiment
$6s6p\ ^1P_1-6s7s\ ^1S_0$	0.015603	0.030421	0.046070	0.044924 [a]
$6s6p\ ^3P_1-6s7s\ ^1S_0$	0.094970	0.103953	0.112577	0.111703
$6s6p\ ^1P_1-6s7s\ ^3S_1$	0.012079	0.021528	0.037090	0.037735
$6s6p\ ^3P_0-6s7s\ ^3S_1$	0.100312	0.102969	0.111303	0.112559
$6s6p\ ^3P_1-6s7s\ ^3S_1$	0.091446	0.095059	0.103597	0.104514
$6s6p\ ^3P_2-6s7s\ ^3S_1$	0.072213	0.076567	0.083389	0.083409

[a]Reference [6].

with nlj spin orbitals covering the same range as above. The number of configurations used was about 2000 for $6s6p\ ^3P_{1,2}$, $^1P_1$, $6s7s\ ^3S_1$ and about 1000 for the remaining states. All core spin orbitals were determined in the single-configuration Dirac-Fock calculations for the ground state $6s^2\ ^1S_0$. The ''frozen-core'' approximation was later assumed. The valence spin orbitals occupied in dominating configuration were generated for each atomic state independently in the single-configuration Dirac-Fock calculations. The virtual (i.e., unoccupied) spin orbitals were calculated separately to minimize the energy of the $\{1s^2\cdots5d^{10}\}nlj$ state of the system's parent ion. This method of generation of virtual orbitals was proposed in our previous study (Stanek et al. [2]) and turned out to be very successful in computations of lowest spin-allowed and spin-forbidden transitions in magnesium isoelectronic sequence. All virtual spin orbitals used in the configuration interaction procedure were the same for the lower and upper states. Transition energies were calculated as differences of total energies of proper states. The Breit interaction is included as a first order perturbation correction to the total energy. The transition probabilities were computed with the theoretical transition energy and using the Babushkin gauge.

The calculated $6s6p-6s7s$ transition energies ΔE as well as transition probabilities A_{ki} are given in Tables I and II, respectively. For triplet-triplet transitions ($6s6p\ ^3P_{0,1,2}-6s7s\ ^3S_1$) correlation effects are not very essential. Our SMDF as well as CIDF transition energies differ here from the experimental values by about 13%. Similarly, the SMDF and CIDF transition probabilities agree reasonably well with the experimental data.

For the $6s6p\ ^1P_1-6s7s\ ^3S_1$, $^1S_0$ and the $6s6p\ ^3P_1-6s7s\ ^1S_0$ transitions where the influence of electron correlation is significant the SMDF transition energies and probabilities are completely erroneous. The CIDF calculations yield here considerably improved values of ΔE but they are still too small in comparison with the experiment. Consequently, transition probabilities are also too small and profoundly differ from the experimental data. The reason for these discrepancies may be the limited basis set used in the CIDF calculations. It causes that representation of the intra-valence and core-valence correlation is not sufficiently accurate. However, further extension of the basis set is not possible because it would make the relativistic configuration interaction calculations too tedious and time consuming. Therefore, we proposed here another approach. This is a configuration interaction method with relativistic wave functions generated using an *ab initio* model potential.

C. Configuration interaction calculations with relativistic wave functions generated using an *ab initio* model potential CIDF(MP)

First, the core spin orbitals were determined in the single-configuration Dirac-Fock calculations for the ground state $6s^2\ ^1S_0$. The ''frozen-core'' approximation was later assumed. Next, both occupied and virtual spin orbitals were generated separately in a single Dirac-Fock calculations to minimize the energy of the $\{1s^2\cdots5d_{3/2}^{4q}5d_{5/2}^{6q}\}nlj$ state of the parent ion where $0<q\leq1$ is a parameter which was adjusted to achieve a minimum of the total energy of a given atomic state (e.g., $6s6p\ ^3P_1$) in configuration-interaction (CI) approach. These spin orbitals were then used to build a CI wave function of the investigated atomic state. The method described above is more elastic than that used previously as it allows for improvement of the field affecting the electron spin orbitals in the generation process.

The form of free parameter in the potential was based on the assumption that correlation effects between core and valence electron affect most profoundly the outermost shell of the core leading to the change in its occupation number similarly to multiconfiguration approach where the square of configuration coefficient multiplied by occupation number can be considered as effective (noninteger) occupation number. Presence of adjustable parameter in the potential used to generate spin orbitals and total CI energy minimum of the

TABLE II. The $6s6p-6s7s$ transition probabilities A_{ki} (in s^{-1}) in HgI (for a description of theoretical methods see text).

Transition	SMDF	CIDF	CIDF(MP)	RPT [a]	Experiment [b]
$6s6p\ ^1P_1-6s7s\ ^1S_0$	3.36×10^6	1.31×10^7	3.05×10^7	$(2.9-3.0)\times10^7$	$(2.71\pm0.14)\times10^7$
$6s6p\ ^3P_1-6s7s\ ^1S_0$	8.88×10^5	1.30×10^6	2.89×10^6	$(6.1-6.9)\times10^5$	$(4.00\pm0.40)\times10^6$
$6s6p\ ^1P_1-6s7s\ ^3S_1$	6.31×10^3	3.24×10^4	1.99×10^5	$(1.2-1.2)\times10^5$	
$6s6p\ ^3P_0-6s7s\ ^3S_1$	1.75×10^7	1.95×10^7	1.81×10^7	$(1.6-1.7)\times10^7$	$(2.07\pm0.20)\times10^7$
$6s6p\ ^3P_1-6s7s\ ^3S_1$	4.63×10^7	5.06×10^7	4.32×10^7	$(4.3-4.7)\times10^7$	$(5.57\pm0.43)\times10^7$
$6s6p\ ^3P_2-6s7s\ ^3S_1$	5.59×10^7	6.03×10^7	5.53×10^7	$(5.2-5.5)\times10^7$	$(4.87\pm0.37)\times10^7$

[a]Reference [8]. (Transition probabilities calculated without and with core-polarization corrections.)
[b]Reference [7].

TABLE III. Comparison of transition energies as well as oscillator strengths for $6s^2\ ^1S_0-6s6p\ ^1P_1$, $^3P_1$ transitions in HgI calculated using different theoretical methods.

Transition	MCRHF+CP [a]	CIRHF+CP [b]	MCRRPA [c]	CIDF	CIDF(MP)	Experiment
			Transition energies			
$6s^2\ ^1S_0-6s6p\ ^1P_1$	0.248324	0.220360		0.230969	0.246500	0.246355[d]
$6s^2\ ^1S_0-6s6p\ ^3P_1$	0.177880	0.159124	0.150060	0.157437	0.179993	0.179576[d]
			Oscillator strengths			
$6s^2\ ^1S_0-6s6p\ ^1P_1$	1.26	1.14		1.30	1.41	1.21 ± 0.09 [e]
						1.18 ± 0.09 [f]
						1.11 ± 0.10 [g]
						1.15 ± 0.11 [h]
$6s^2\ ^1S_0-6s6p\ ^3P_1$	1.98×10^{-2}	2.86×10^{-2}	1.95×10^{-2}	6.96×10^{-2}	2.45×10^{-2}	$(2.41\pm0.02)\times10^{-2}$ [i]
						$(2.37\pm0.08)\times10^{-2}$ [j]
						$(2.49\pm0.10)\times10^{-2}$ [k]
						$(2.47\pm0.04)\times10^{-2}$ [l]
						$(2.90\pm0.60)\times10^{-2}$ [m]

[a]Reference [3].
[b]Reference [4].
[c]Reference [5].
[d]Reference [6].
[e]Reference [9].
[f]Reference [10].
[g]Reference [11].

[h]Reference [12].
[i]Reference [13].
[j]Reference [14].
[k]Reference [15].
[l]Reference [16].
[m]Reference [17].

system under consideration adopted as criterion of the parameter choice enable us to treat the proposed method as an *ab initio* model potential approach to determination of spin orbitals used to construct CI wave functions. According to our calculations the values of q corresponding to total CI energy minimum are 0.51, 0.58, and 0.60 for $6s^2\ ^1S_0$, $6s6p\ ^3P_1$, and $6s6p\ ^1P_1$, respectively, whereas the value of $q=1.00$ corresponds to our previously used CIDF method. To take into account intravalence as well as core-valence electron correlation the same basis set was used as in the CIDF calculations. On the other hand, using the same basis set allows us to compare both methods.

To test this method we calculated excitation energies ΔE and oscillator strengths f for the $6s^2\ ^1S_0-6s6p\ ^1P_1$, $^3P_1$ transitions in HgI because these data are quite well known. We compared our CIDF and CIDF(MP) results (Table III) with values from the multiconfiguration relativistic Hartree-Fock (MCRHF) calculations (Migdalek and Baylis [3]) with core-valence electron correlation accounted for in a core-polarization (CP) model, the limited configuration interaction relativistic Hartree-Fock with core polarization (CIRHF+CP) approach (Migdalek and Bojara [4]) and the multiconfiguration relativistic random-phase approximation (MCRRPA) (Chou *et al.* [5]) as well as with the experiment. For both transitions our CIDF(MP) excitation energies are in excellent agreement with the experimental values whereas other theoretical methods yield worse result. Similarly, the CIDF(MP) oscillator strength for the forbidden transition is in very good agreement with the experimental data whereas for the resonance transition our f value is slightly larger than the experimental result. This comparison shows that the

CIDF(MP) method yields, for transitions considered, results in much better agreement with experiment than those obtained with the CIDF version formerly used by us.

In order to evaluate the convergence of both CIDF and CIDF(MP) approaches we had tested them in two types of calculations differing in length of basis sets. In the first type, all single and double excitations up to $9p$ (except of $6f$, $7f$, $8f$ and $7d$, $8d$ orbitals) had been included. In the second type we extended the basis set up to $10p$ orbital. The number of configurations used increased from 1952 to 2925 for the $6s6p\ ^3P_1$, $^1P_1$ states and from 731 to 1063 for the $6s^2\ ^1S_0$ state. Such extension resulted for the CIDF method in a change of $6s^2\ ^1S_0-6s6p\ ^1P_1$ excitation energy from 0.23103350 a.u. to 0.23113760 a.u., whereas for the $6s^2\ ^1S_0-6s6p\ ^3P_1$ excitation energy the corresponding change was from 0.15756750 a.u. to 0.15771780 a.u. For the CIDF(MP) method extended calculations yielded 0.24713490 a.u. instead of 0.2470950 a.u. for the $6s^2\ ^1S_0-6s6p\ ^1P_1$ transition and 0.17969310 a.u. instead of 0.17962050 a.u. for the $6s^2\ ^1S_0-6s6p\ ^3P_1$ transition. Since the experimental values are 0.246355 a.u. and 0.179576 a.u., respectively, it can be seen that it is the CIDF(MP) method which converges to the values close to experimental excitation energies, whereas the CIDF converges to the much less accurate values.

III. DISCUSSION OF RESULTS

The $6s6p-6s7s$ transition energies ΔE and probabilities calculated with all three methods are presented in Tables I and II, respectively, and compared with available experimen-

tal and theoretical data. The experimental transition energies were taken from tables by Moore [6], whereas experimental transition probabilities are those published by Benck *et al.* [7]. The only existing other theoretical transition probabilities for transitions considered here, to our knowledge, are those obtained by Hafner and Schwarz [8] with semiempirical relativistic pseudopotential approach RPT.

The $6s6p–6s7s$ transition array can be divided in two groups: triplet-triplet and remaining transitions. As was already mentioned, for triplet-triplet transitions correlation effects are not decisive and both single-manifold SMDF and our earlier configuration-interaction CIDF methods give similar results for both energies and transition probabilities, all in reasonably good agreement with experimental data. However even for these transitions, our CIDF(MP) method yields clearly improved transition energies in comparison with experiment. In light of the above slightly better agreement of CIDF or even SMDF transition probabilities with experiment observed for $6s6p$ $^3P_0$, $^3P_1–6s7s$ $^3S_1$ transitions seems to be rather fortuitous because both SMDF and CIDF methods give here clearly worse transition energies.

For remaining transitions and particularly for $6s6p$ $^1P_1–6s7s$ $^3S_1$, $^1S_0$ transitions electron correlation effects play dramatic role for both transition energies and transition probabilities. As pointed out earlier, even the configuration-interaction CIDF method is not sufficient here and good agreement with experimental data for both transition energies and probabilities is achieved only when our new CIDF(MP) method is employed. For most cases the CIDF(MP) transition probabilities agree favorably with semiempirical pseudopotential results of Hafner and Schwarz [8]. The only exception is the $6s6p$ $^3P_1–6s7s$ $^1S_0$ transition where their data ($6.1\times10^5–6.9\times10^5$ without and with core polarization, respectively) differ from the experimental value (4.0×10^6) by one order of magnitude, whereas our CIDF(MP) result is 2.89×10^6.

In our opinion, present study demonstrates that the influence of intravalence as well as core-valence electron correlation on the transition probabilities and transition energies is very essential at least for some transitions of $6s6p–6s7s$ transition array. We have proposed here a method of generation of spin orbitals for the configuration interaction approach that seems to be more effective at the same basis set used.

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