Core effects on ionization potentials in thallium

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Ionization potentials (IP's) are evaluated for various excited states of Tl using the relativistic coupled cluster (CCCD) theory in the even-parity pair channel approximation (CCSD-EPC). An average accuracy below half a percent is reached. The effect of deep core electrons on the core-valence correlations is investigated. It is found that electrons in the third subshell ($n=3$) modify the IP's of the $6p$ orbitals by 100 cm^{-1}. By comparison with calculations made in the linearized CCSD (LCCSD) approximation it is demonstrated that nonlinear contributions are mandatory to reach an accuracy below half a percent for the $6p_{1/2}$ orbital.

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I. INTRODUCTION

Thallium is among the prime candidates for the study of parity nonconservation (PNC) in atoms as a test of the standard model of elementary particle physics. The latest measurement of the optical rotation in that atom arising from the interference of the PNC induced electric dipole (E1PNC) and magnetic dipole (M1) amplitudes for the $6p_{1/2}\rightarrow 6p_{3/2}$ transition has reached an accuracy of 1% [1], whereas the most advanced calculation of the E1PNC transition amplitude, based on a variant of the many-body perturbation theory, has an accuracy of about 3% [2].

The E1PNC transition amplitude depends on the interplay of the neutral weak current interaction and the electromagnetic interaction between the electrons in an atom. The former interaction is limited to the nuclear region and therefore takes place predominantly between the nucleus and the s and $p_{1/2}$ electrons of both core and virtual orbitals. The effect of correlation of these electrons with other electrons must be taken into account as accurately as possible for a high precision calculation of the E1PNC transition amplitude. In a previous work [3] we have investigated the contribution of deep core electrons to the correlation energy of Tl^+ using the LCCSD approximation. It was found that electrons of the third subshell ($n=3$) contribute almost 20% to the correlation energy. In the present work we extend the investigation to IP's and include nonlinear terms in the CC equations.

Eliav *et al.* [4] have obtained an ionization energy of the Tl groundstate of high accuracy with the help of CC. The best theoretical results for IP's of Tl have been achieved by Dzuba *et al.* [5]. In their work, based on an a hybrid of many-body perturbation theory (MBPT) and configuration interaction (CI), they could reach a remarkable accuracy of less than 0.2%, however, with the help of an adjustable energy shift which has been fitted to match the experimental energy spectrum as closely as possible. Their method is thus not purely *ab initio*.

In contrast, the CC method, being an all order many-body theory [6–10], is a fully *ab initio* approach. It is also size extensive and therefore a natural choice for high precision computations on heavy atoms. However, the computational demands of the relativistic CC approach represent a formidable challenge and so far they have stood in the way of extensive computations on atoms as heavy as Tl. Our present work, which exploits the remarkable features of coupled cluster theory and modern parallel programming techniques, could open the way for large scale computations on very heavy atoms in a way that the many-body interactions involving the core electrons can be taken into account to very high accuracy. This would be an important step forward in the computation of atomic properties like PNC and hyperfine interactions that strongly depend on the core electrons.

II. METHODOLOGY

In the closed shell CC approach, we start with the n-electron Dirac-Fock (DF) reference state $|\Phi\rangle$ and write the exact ground state as

$$|\Psi\rangle = e^T|\Phi\rangle, \tag{1}$$

where T is the core electron excitation operator. The Schrödinger equation

$$He^T|\Phi\rangle = Ee^T|\Phi\rangle \tag{2}$$

leads to the exact ground state energy E. However, it is technically simpler to first define the normal ordered Hamiltonian

$$\tilde{H} \equiv H - \langle\Phi|H|\Phi\rangle = H - E_{DF}, \tag{3}$$

with the DF energy E_{DF} and solve the modified Schrödinger equation

$$\tilde{H}e^T|\Phi\rangle = (E - E_{DF})e^T|\Phi\rangle \equiv E_{corr}e^T|\Phi\rangle. \tag{4}$$

After premultiplication with e^{-T} and projecting on $\langle\Phi|$ we obtain the correlation energy

$$\langle\Phi|\overline{H}|\Phi\rangle = E_{corr}, \tag{5}$$

where we have defined the dressed, normal ordered Hamiltonian

$$\overline{H} = e^{-T} \tilde{H} e^{T}. \tag{6}$$

By projecting onto any of the excited determinants $\langle \Phi^* |$ we additionally find the set of equations

$$\langle \Phi^* | \overline{H} | \Phi \rangle = 0. \tag{7}$$

Equations (5) and (7) are the coupled cluster equations. In a first step, the set of equations (7) has to be solved to yield the cluster operator T, which then can be used to define the dressed Hamiltonian $\overline{H}$ and to evaluate the correlation energy E_{corr}. In the CCSD (coupled cluster singles and doubles) approximation, the cluster operator T is composed of one- and two-body excitation operators, i.e., $T = T_1 + T_2$, which are expressed in terms of second quantization, and after contraction of the ladder operators [11] and rearranging the indices, Eq. (7) can be expressed in the following matrix form:

$$A + B(T) \cdot T = 0, \tag{8}$$

where A is a constant vector which consists of the elements $\langle \Phi^* | \tilde{H} | \Phi \rangle$ and T is the vector of the excitation amplitudes. The matrix $B(T)$ itself depends on the cluster amplitudes so that Eq. (8) has to be solved in an iterative procedure.

Due to the spherical symmetry of atoms, the above derived equations can be separated into a radial and an angular part, which considerably reduces the numerical effort. The radial Coulomb integrals, which define the most time consuming part of the computation, can be stored in RAM whereas the angular parts, which consist of much simpler algebraic expressions, can be evaluated on the fly. In our calculations we made use of the CCSD-EPC approximation, which reduces the number of cluster amplitudes by a factor 1/2 with the help of selection rules in the angular part of the cluster amplitudes. Details about the angular reduction [12–16] and the CCSD-EPC approximation [17,3] can be found elsewhere.

The groundstate of Tl contains only one valence electron in the $6p_{1/2}$ orbital. One way to evaluate the groundstate energy of Tl is to first compute the correlations within the closed shell system Tl^+ using the closed shell CC approach and then add another electron to the $6p_{1/2}$ orbital with the help of the open shell CC (OSCC) technique [16]. Similarly, the valence electron can be added to any other virtual orbital to yield excitation energies. In order to add an electron to the kth virtual orbital of the DF reference state we define

$$|\Phi_k^{n+1}\rangle \equiv a_k^\dagger |\Phi\rangle \tag{9}$$

with the help of the particle creation operator $a_k^\dagger$. We now define the exact state using excitation operators for both the core electrons and the valence electron in the following way:

$$|\Psi_k^{n+1}\rangle = e^T \{e^{S_k}\} |\Phi_k^{n+1}\rangle, \tag{10}$$

where $\{S_k\}$ is the normal ordered valence electron excitation operator [15]. Since S_k has to contain the particle anihilation operator a_k, it cannot, due to the normal ordering, be connected with any other valence electron excitation operator so that $\{e^{S_k}\}$ reduces to $(1+S_k)$ and we can rewrite Eq. (10) as

$$|\Psi_k^{n+1}\rangle = e^T (1+S_k) |\Phi_k^{n+1}\rangle. \tag{11}$$

Following the same procedure as in the closed shell approach, we obtain a set of equations

$$\langle \Phi_k^{n+1} | \overline{H} (1+S_k) | \Phi_k^{n+1} \rangle = \Delta E_k \tag{12}$$

and

$$\langle \Phi_k^{*,n+1} | \overline{H} (1+S_k) | \Phi_k^{n+1} \rangle = \Delta E_k \langle \Phi_k^{*,n+1} | S_k | \Phi_k^{n+1} \rangle. \tag{13}$$

Here, ΔE_k is the difference between the energy of the closed shell state Ψ and the single valence state Ψ_k^{n+1}, i.e., the energy which is released when an electron is attached to the kth virtual orbital of the closed shell state. Equation (13) is nonlinear in S_k because the energy difference ΔE_k itself is a function of S_k. To solve the set of equations, one has to start with an initial estimate for the S_k amplitudes, e.g., $S_k = 0$, evaluate the energy difference using Eq. (12) and put the result into Eq. (13) to solve for the S_k amplitudes. This procedure has to be iterated and driven to self-consistence.

III. COMPUTATION

In the actual computation, the DF ground state of Tl^+ was evaluated using the finite basis set expansion method (FBSE) [18] with a large basis set of $(30s25p20d15f15g)$ Gaussian functions of the form

$$F_{i,k}(r) = r^k e^{-\alpha_i r^2} \tag{14}$$

with $k = 0,1,\ldots$ for s, p, $\ldots$ type functions, respectively. For the exponents, the universal even tempering condition

$$\alpha_i = \alpha_{i-1} \beta, \quad i = 1, \ldots, N, \tag{15}$$

was applied. Here, N is the number of basis functions for a specific symmetry. To define the basis, two parameters, α_o and β, had to be specified. As in our previous work [3], we have used $\alpha_o = 0.007\,25$ and $\beta = 2.73$ for all symmetries. The self-consistent DF orbitals were stored on a grid. It is known from previous work that virtual orbitals with high energies do not contribute significantly to properties like IP's [4]. In the CCSD calculations, we have therefore truncated the virtual orbital space to orbitals with less than 100 a.u., which implies that s, p, d and f orbitals up to the 12th subshell were included. On the DF level 15 g orbitals were used, but in the CC calculations only the lowest 5 of them were included.

In order to examine the core effects on the IP's, the inner core subshells have been included one by one into the closed shell CCSD calculation. In the basis denoted as Tl_b, only the $5s$, $6s$, $5p$, $5d$ and $4f$ core electrons were correlated. In Tl_c, the $4s$, $4p$ and $4d$ orbitals were added, and in Tl_d also

TABLE I. IP's of Tl (in cm^{-1}) using different sets of correlated core orbitals. In the Tl_b basis, only the two outer s and the most outer p, d and f core-orbitals were correlated. In Tl_c, the complete subshell ($n=4$) and in Tl_d also the subshell ($n=3$) were included. The virtual space contains s,p,d,f orbitals up to the subshell ($n=12$) and additionally 5 g orbitals. Dzuba's accurate results are obtained by a semi-*ab-initio* approach.

System	Tl_b (LCCSD)	Tl_b	Tl_c	Tl_d	Expt. [a]	Dzuba [b]
Core	$5s6s5p5d4f$	*ibid.*	$+4s4p4d$	$+3s3p3d$		Full core
$6p_{1/2}$	48592	48827	48909	49022	49264	49264
$6p_{3/2}$	41217	41281	41357	41455	41471	41456
$7s_{1/2}$	22874	22864	22852	22844	22787	22792
$6d_{3/2}$	13212	13208	13199	13196	13146	13146
$6d_{5/2}$	13080	13091	13082	13077	13064	13042
$7p_{1/2}$	15012	15027	15022	15023	15104	15095
$7p_{3/2}$	14046	14039	14038	14041	14103	14094

[a]As quoted in [2].
[b]Reference [5].

the $3s$, $3p$ and $3d$ electrons. The closed shell CC computations were performed at CDAC's (Center for Development of Advanced Computing) National PARAM Supercomputing Facility in Pune. To solve the nonlinear CCSD equations for Tl_d with 280 000 cluster amplitudes, five CPU-months on Sun Ultra Sparc processors (400 MHz) were required. The OSCC calculations were less expensive and could be done on a local Sun E450 Server.

IV. RESULTS

Table I displays the results for the ionization potentials of various orbitals and different basis sets. As a comparison, experimental data and the best available theoretical results obtained by Dzuba *et al.* [5] are given. For the Tl_b basis, also results obtained by the LCCSD approximation are given.

With an increasing number of core electrons, the IP results for the $6p$ orbitals improved significantly. The other orbitals, however, did exhibit a less significant dependence on the amount of correlated core electrons. Also remarkable is the fact that the $6p_{1/2}$ orbital improved a lot (0.5%) with the inclusion of the nonlinear equations as explicitly demonstrated in the Tl_b calculation, whereas for all other orbitals the nonlinear contributions turned out to be rather marginal, namely of the order of 0.1%. To understand this behavior one has to keep in mind that the Tl core extends up to the $6s$ orbitals. The $6p$ orbitals, being in the same subshell, overlap strongly with $6s$ and as a consequence the core-valence correlations are especially pronounced for these orbitals. This implies that an accurate evaluation of the $6p$ IP's requires an accurate treatment of the core correlations, and the calculations prove that even the subshell ($n=3$) leads to an improvement of the IP's by 100 cm^{-1}. In the case of the $6d$ orbitals and the $7s$ orbital, the overlap with the core is much less, leading to an improvement of the order of 10 cm^{-1} with increasing core correlations. For the $7p$ electrons, no improvement is visible at all, indicating that the overlap of the $7p$ orbitals with the core is already negligible.

Among all valence orbitals, the $6p_{1/2}$ has the strongest overlap with the $6s$ core orbital. The core-valence correlations are especially large and therefore the nonlinear contributions become significant, which leads to the observed improvement of the IP result using the nonlinear CCSD method. It therefore appears to be mandatory to perform nonlinear CCSD calculations in order to reach an accuracy of half a percent for the IP of the $6p_{1/2}$ orbital. For all other orbitals, however, the LCCSD approximation yields results which are remarkably close to the results obtained in the full CCSD calculations.

In comparison with the experimental results, the IP values have reached an accuracy of 0.5% or better. These are not the most accurate theoretical numbers available, as the comparison with the results of Dzuba *et al.* [5] demonstrates. To yield results of high accuracy, they exploit a technique which is a hybrid of MBPT and CI. The MBPT part produces an effective Hamiltonian which represents the core part of the system. Along with that, an adjustable energy shift can be chosen on the grounds of best agreement between the calculated energy spectrum and the experimentally observed spectrum. In contrast to the CC approach, Dzuba's effective operator approach is not fully *ab initio*, but much less computationally demanding.

In order to increase further the accuracy of the IP results, the virtual space has to be increased significantly. Dzuba used basis functions up to h symmetry and the same should be done in the CC approach, too. This is likely to improve the accuracy especially of the higher lying orbitals like $7p$ and above, which are also well decoupled from the core so that it would be adequate to freeze most of the core orbitals in order to save CPU time. However, it was not the purpose of this article to get the most accurate results for the IP's, but instead to investigate the significance of core-valence correlations to the IP's. The results suggest that in order to obtain a high precision for the $6p$ orbitals, which is mandatory to evaluate the PNC transitions $6p_{1/2} \rightarrow 6p_{3/3}$ and $6p_{1/2} \rightarrow 7s_{1/2}$, both the number of core orbitals as well as the number of virtual orbitals have to be large. Unfortunately, the LCCSD approximation appears to be insufficient exactly

for the $6p_{1/2}$ orbital, so that fully nonlinear calculations are unavoidable. This is a problem which will be demanding from the computational but not from the methodological point of view. Experiments have shown that the CCSD equations are very efficiently parallelizable and scale well up to a large number of processors, so that with the help of nowadays massive parallel supercomputers this problem appears to be tractable.

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