Relativistic general-order coupled-cluster method for high-precision calculations: Application to the Al\(^{+}\) atomic clock

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We report the implementation of a general-order relativistic coupled-cluster method for performing high-precision calculations of atomic and molecular properties. As a first application, the black-body radiation shift of the \(\text{Al}^{+}\) clock transition has been estimated precisely. The computed shift relative to the frequency of the \(3\times10^3\,1S_0^+ \rightarrow 3\times3\,P_0^0\) clock transition given by \((-3.66 \pm 0.60) \times 10^{-18}\) calls for an improvement over the recent measurement with a reported result of \((-9 \pm 3) \times 10^{-18}\) [Phys. Rev. Lett. 104, 070802 (2010)].

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The role of high-precision calculations of various properties of heavy atoms and molecules which support the state-of-the-art measurements has gained incredible importance in recent years. This is particularly true in the context of the latest measurements have gained incredible importance in recent years. This is particularly true in the context of the BBR shift in the Al\(^{+}\) clock transition given by \((-3.66 \pm 0.60) \times 10^{-18}\) calls for an improvement over the recent measurement with a reported result of \((-9 \pm 3) \times 10^{-18}\) [Phys. Rev. Lett. 104, 070802 (2010)].

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The exact wave function in the single-reference (SR) CC theory involves an exponential parametrization of the form

\[
|\Psi_{\text{CC}}\rangle = e^\mathcal{T} |0\rangle,
\]

where \(|0\rangle\) is the Dirac-Hartree-Fock (DHF) reference determinant, and the cluster operator \(\mathcal{T}\) can be decomposed as \(\mathcal{T} = \sum_{a=1}^n \mathcal{T}_a\), where

\[
\mathcal{T}_a = \sum_{\alpha_1 < \cdots < \alpha_k} \tau^{\alpha_1 \cdots \alpha_k}_{\beta_1 \cdots \beta_k} a_1^{\dagger} i_1^{\dagger} a_2^{\dagger} i_2^{\dagger} \cdots a_k^{\dagger} i_k^{\dagger}.
\]

The convention followed here is that indices \(i (a)\) refer to occupied (virtual) spinors in the reference determinant. Projecting onto the excited determinants defined by \(|\Psi^{\alpha_1 \cdots \alpha_k}_{\beta_1 \cdots \beta_k}\rangle\) we get the nonlinear algebraic equations for the correlation energy \(E\) and unknown cluster amplitudes \(\tau^{\alpha_1 \cdots \alpha_k}_{\beta_1 \cdots \beta_k}\) for the excitation of any order as

\[
\langle \Psi^{\alpha_1 \cdots \alpha_k}_{\beta_1 \cdots \beta_k} | e^{-\mathcal{T} \hat{H}_N} e^{\mathcal{T}} |0\rangle = E \delta_{k,0}, \quad (k = 0, \ldots, n),
\]

where \(\hat{H}_N\) is the normal-ordered Dirac-Coulomb (DC) Hamiltonian and \(k\) is the level of excitation. The CC approaches correspond to the \(n = 2, 3, 4, \ldots,\) values, i.e., the CC singles and doubles (CCSD), CC singles, doubles, and triples (CCSDT), CC singles, doubles, triples, and quadruples (CCSDTQ), etc., methods constitute a hierarchy, which converges to the exact solution of the Dirac equation in the given one-particle basis set.

The excitation energies are obtained invoking the LR CC theory as given in Refs. [16,17]. In LR CC theory the excitation energies \(\omega\) are calculated by determining the right-hand eigenvalues of the CC Jacobian as

\[
\langle \Psi^{\alpha_1 \cdots \alpha_k}_{\beta_1 \cdots \beta_k} | (e^{-\mathcal{T} \hat{H}_N} e^{\mathcal{T}} \hat{R}) |0\rangle = \omega \tau^{\alpha_1 \cdots \alpha_k}_{\beta_1 \cdots \beta_k},
\]

where operator \(\hat{R}\) has the same structure as the cluster operator with parameters \(\tau^{\alpha_1 \cdots \alpha_k}_{\beta_1 \cdots \beta_k}\).

With the newly developed general-order relativistic CC code we can handle a variety of methods including SR CC approaches for arbitrary high-\(n\) values as well as a state-selective multireference (MR) CC ansatz based on the SR CC
In comparison to the existing relativistic CC [2–6,8], many-body perturbation theory (MBPT) [13], and CI [12,15] methods the new approaches offer the following new features and advantages: (i) previously only single, double, and approximate triple excitations could be considered in CC or MBPT methods, our implementation allows for arbitrary high excitations and thereby higher accuracy; (ii) in contrast to linearized CC or MBPT methods no approximations are introduced in the equations, that is, all diagrams are retained and treated iteratively; (iii) the LR theory, which enables the balanced description of the ground and excited states and facilitates the calculation of numerous properties, has not been implemented so far for relativistic CC methods; (iv) the new methods are applicable to the ground and excited states of any multiplicity of atoms and molecules and are not confined, e.g., to one-valence systems or one-hole and one-particle excited states; (v) in contrast to CI approaches CC methods truncated to one-valence systems or one-hole and one-particle excited multiplicity of atoms and molecules and are not confined, e.g., methods are applicable to the ground and excited states of any size and designed such that they systematically converge to the complete basis-set limit. The CC calculations were carried out with our new all-order relativistic CC code implemented in the MRCC suite [21]. The molecular orbital integrals were generated by the DIRAC package [22].

To give an accurate estimate of the properties studied, we have adopted a composite scheme, which is well established in quantum chemistry and has widely been used for highly accurate calculations of atomic and molecular properties (see, Consequently the evaluation of the BBR shift requires the knowledge of the static polarizabilities for the two states involved in the clock transition. It is obvious from Eq. (5) that the static polarizability can be evaluated as the second derivative of \( E_i(\varepsilon) \) with respect to \( \varepsilon \). In our study we followed this approach and calculated the polarizabilities by numerical differentiation. The total energies were computed with and without the perturbation; here the perturbation was taken to be \(-D \cdot \varepsilon\) where \( D\) is the induced electric dipole moment, and the values of the electric field \( \varepsilon \) were fixed to \(1 \times 10^{-3}\) and \(2 \times 10^{-3}\) a.u. The polarizabilities were obtained from the resulting three energy values assuming that they lie on a quartic polynomial. With test calculations the numerical error of this procedure was found to be negligible.

In order to approach the exact solution of the Dirac equation with the Dirac-Coulomb Hamiltonian for the Al\(^+\) ion as closely as possible, the convergent hierarchy of CC methods was combined with the convergent basis sets in the total energy calculations. The ground-state energies were obtained using the CCSD, CCSDT, and CCSDTQ methods, while excited-state energies were determined by the LR CC method in the same excitation manifold. The one-electron basis sets used were Dunning's uncontracted correlation consistent double-, triple-, quadruple-, and pentuple-\(\xi\) sets with polarization and core-valence correlation functions and augmented with three diffuse functions in each symmetry considered [19,20]. These basis sets are hereafter simply referred to as \(X\xi\) where \(X = 2, 3, 4,\) and 5, respectively. These hierarchical basis sets, whose details are shown in Table I, are of progressively larger sizes and designed such that they systematically converge to the complete basis-set limit. The CC calculations were carried out with our new all-order relativistic CC code implemented in the MRCC suite [21]. The molecular orbital integrals were generated by the DI RAC package [22].

As is well known, the energy of the \(i\)th state of an atom placed in an isotropic electric field of strength \( \varepsilon \) changes as

\[
E_i(\varepsilon) = E_i(0) - \frac{\alpha_i}{2} \varepsilon^2 - \cdots, \tag{5}
\]

where \( E_i(0) \) and \( E_i(\varepsilon) \) are the total energies of the state \(i\) in the absence and the presence of the field, respectively, and \( \alpha_i \) is the static dipole polarizability of state \(i\). The BBR shift for a transition \(|J_i,M_i\rangle \rightarrow |J_f,M_f\rangle\) is the shift of the corresponding transition energy due to the finite background thermal radiation. At temperature \(T\), neglecting the dynamic correction factor from Mitroy et al. [12], in the adiabatic expansion it is given by

\[
\Delta E_{ij}^{\text{BBR}} = \frac{1}{2}(831.9 \text{ V/m})^2 \left( \frac{T(K)}{300} \right)^4 (\alpha_i - \alpha_j). \tag{6}
\]

Consequently the evaluation of the BBR shift requires the knowledge of the static polarizabilities for the two states involved in the clock transition.

It is obvious from Eq. (5) that the static polarizability can be evaluated as the second derivative of \( E_i(\varepsilon) \) with respect to \( \varepsilon \). In our study we followed this approach and calculated the polarizabilities by numerical differentiation. The total energies were computed with and without the perturbation; here the perturbation was taken to be \(-D \cdot \varepsilon\) where \(D\) is the induced electric dipole moment, and the values of the electric field \(\varepsilon\) were fixed to \(1 \times 10^{-3}\) and \(2 \times 10^{-3}\) a.u. The polarizabilities were obtained from the resulting three energy values assuming that they lie on a quartic polynomial. With test calculations the numerical error of this procedure was found to be negligible.

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To give an accurate estimate of the properties studied, we have adopted a composite scheme, which is well established in quantum chemistry and has widely been used for highly accurate calculations of atomic and molecular properties (see,
e.g., Ref. [23]). In this approach any property $P$, i.e., excitation energy, polarizability, or differential polarizability, is evaluated as

$$\Delta P = P_{\text{CCSD}} + \Delta P_T + \Delta P_Q + \Delta P_{\text{BQ}},$$

where $\Delta P_T = P_{\text{CCSDT}} - P_{\text{CCSD}}$, $\Delta P_Q = P_{\text{CCSDTQ}} - P_{\text{CCSDT}}$, while $P_{\text{CCSD}}$, $P_{\text{CCSDT}}$, and $P_{\text{CCSDTQ}}$ are the values calculated for property $P$ using the CCSD, CCSDT, and CCSDTQ methods, respectively. $\Delta P_{\text{BQ}}$ is the contributions from the Breit interaction and QED corrections. We will simply denote the $P_{\text{CCSD}}$, $\Delta P_T$, and $\Delta P_Q$ values computed with an $X\xi$ basis set as $P_{\text{CCSD}}|_{X\xi}$, $\Delta P_T|_{X\xi}$, and $\Delta P_Q|_{X\xi}$, respectively. The latter three contributions are calculated with the largest feasible basis set and the largest feasible number of correlated electrons. In our study, the $P_{\text{CCSD}}$ and $\Delta P_T$ were computed with the 5$\xi$ and 3$\xi$ basis sets, respectively, correlating all electrons and all orbitals. The evaluation of $\Delta P_Q$ was only feasible with the 2$\xi$ basis set, but further approximations were necessary even in this basis, and the 1$s$ and 2$s$ electrons were frozen as well as the virtual orbitals lying above 5$E_H$ were dropped. The $\Delta P_{\text{BQ}}$ correction was estimated using the numerical multiconfigurational Dirac-Fock (MCDF) method as implemented in the MCDGFME program [24] and the sum-over-states expression for polarizabilities [12].

The results of CC calculations with various basis sets are compiled in Table I, while the calculation of the investigated properties using the composite approach is detailed in Table II. The convergence of both the excitation energies and polarizabilities with increasing level of correlation is rapid. The convergence of both the excitation energies and polarizability properties using the composite approach is detailed in Table II. The latter three contributions are calculated with the largest feasible basis set and the largest feasible number of correlated electrons. In our study, the $P_{\text{CCSD}}$ and $\Delta P_T$ were computed with the 5$\xi$ and 3$\xi$ basis sets, respectively, correlating all electrons and all orbitals. The evaluation of $\Delta P_Q$ was only feasible with the 2$\xi$ basis set, but further approximations were necessary even in this basis, and the 1$s$ and 2$s$ electrons were frozen as well as the virtual orbitals lying above 5$E_H$ were dropped. The $\Delta P_{\text{BQ}}$ correction was estimated using the numerical multiconfigurational Dirac-Fock (MCDF) method as implemented in the MCDGFME program [24] and the sum-over-states expression for polarizabilities [12].

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The error bars of our computed values were estimated as follows on the basis of the convergence of the calculated properties shown in Table I. Let us consider first the $P_{\text{CCSD}}$ term which can be divided into the Hartree-Fock and the correlation contributions. It has been proven in numerous studies (see, e.g., Refs. [25] and [26]) that when using the $X\xi$ ($X \geq 3$) correlation-consistent basis sets the first contribution converges exponentially to the infinite basis-set limit. This similarity holds for the correlation contribution if $X \leq 5$, while its convergence slows down with the larger basis sets. In practice, if $P_{\text{CCSD}}$ is evaluated with the $X\xi$, $(X + 1)\xi$, and $(X + 2)\xi$ basis sets, the $[P_{\text{CCSD}}|_{X\xi} - P_{\text{CCSD}}|_{(X + 1)\xi}]/[P_{\text{CCSD}}|_{X\xi} - P_{\text{CCSD}}|_{(X + 2)\xi}]$ ratio is considerably larger than two if $X = 3$, and it is close to two with larger basis sets (see, e.g., Refs. [26] and [17]). Let us simply suppose that the above quotient is equal to two, then the error of $P_{\text{CCSD}}|_{X\xi}$ with respect to the hypothetical $P_{\text{CCSD}}$ value computed in the infinite basis is identical to $P_{\text{CCSD}}|_{X\xi} - P_{\text{CCSD}}|_{(X + 1)\xi}$ since the sum of the $1/2 + 1/4 + \cdots$ series is one. This reduction of the basis-set error would also be valid for the current properties. In fact, the ratio of the $P_{\text{CCSD}}|_{4\xi} - P_{\text{CCSD}}|_{3\xi}$ and $P_{\text{CCSD}}|_{5\xi} - P_{\text{CCSD}}|_{4\xi}$ differences for excitation energies, ground- and excited-state polarizabilities, and polarizability shifts is 2.7, 5.8, 7.8, and 22.1, respectively. Thus we presume that twice the $P_{\text{CCSD}}|_{5\xi} - P_{\text{CCSD}}|_{4\xi}$ difference is a conservative estimate for the basis set error of the $P_{\text{CCSD}}|_{5\xi}$ values, and we attach these numbers as error bars. The convergence of $\Delta P_T$ with the basis set is known to be similar to that of the correlation contribution to $P_{\text{CCSD}}$ [26]. Therefore we take again $2 \times (\Delta P_T|_{3\xi} - \Delta P_T|_{2\xi})$ as a conservative choice for the error. The $\Delta P_Q$ contributions are only available in one basis set, thus no conclusion about their basis-set dependence can be drawn. Previous experience shows (see, e.g., Ref. [23]) that the error of this contribution computed even with the small 2$\xi$ basis set is never in error by more than 50% with respect to the basis-set limit. Nevertheless, to be conservative, we take twice the entire contribution as the error bar. As to the accuracy of the $\Delta P_{\text{BQ}}$ contribution we remark that it is computed using numerical orbitals at the MCDF level of the theory and hence it is devoid of any basis-set

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Excitation energy</th>
<th>$3\xi^2 1S_0^+$</th>
<th>$3\xi 3p^2 P_0^+$</th>
<th>Differential</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{CCSD}}$</td>
<td>37186 ± 52</td>
<td>24.251 ± 0.044</td>
<td>24.656 ± 0.088</td>
<td>0.406 ± 0.042</td>
<td>5$\xi$ basis set</td>
</tr>
<tr>
<td>$\Delta P_T$</td>
<td>146 ± 33</td>
<td>-0.126 ± 0.011</td>
<td>-0.061 ± 0.015</td>
<td>0.065 ± 0.026</td>
<td>3$\xi$ basis set</td>
</tr>
<tr>
<td>$\Delta P_Q$</td>
<td>2 ± 4</td>
<td>-0.002 ± 0.005</td>
<td>0.001 ± 0.002</td>
<td>0.003 ± 0.007</td>
<td>2$\xi$ basis set</td>
</tr>
<tr>
<td>$\Delta P_{\text{BQ}}$</td>
<td>-6 ± 6</td>
<td>0.015 ± 0.015</td>
<td>0.018 ± 0.018</td>
<td>0.003 ± 0.003</td>
<td>Numerical MCDF</td>
</tr>
<tr>
<td>Composite</td>
<td>37326 ± 95</td>
<td>24.137 ± 0.075</td>
<td>24.614 ± 0.123</td>
<td>0.477 ± 0.078</td>
<td>Sum of all contributions</td>
</tr>
</tbody>
</table>
Incompleteness errors. As the missing correlation contribution to this correction is not expected to exceed its MCFD value, we have taken the entire value itself as the upper limit of the error.

For the excitation energy a highly accurate experimental value, 37 393 ± 0 cm⁻¹ is available [1], thus the agreement between the experimental and our best calculated excitation energy, 37 326 ± 95 cm⁻¹ is very good and the deviation is within 0.2% of the experimental energy.

We compare our polarizabilities and relative BBR shift (defined by the quotient of the BBR shift and the clock frequency) to the previous theoretical and empirical results in Table III. Our results are in good agreement with the previous computational results, however, more precise than the latter. In contrast, there is a considerable discrepancy between the present and the experimental BBR shift. There is a brief discussion on various approaches employed to calculate the polarizabilities and the BBR shift by Mitroy et al. [12], hence we do not repeat them here, however, we would like to emphasize that our results are the first ab initio values based on a relativistic framework.

In conclusion, we have developed a general-order relativistic coupled-cluster method for high-precision calculations in atoms and molecules. Using this method the ground-state, excited-state, and differential polarizabilities of the Al⁺ ion are obtained to be 24.14 ± 0.08, 24.61 ± 0.12, and 0.48 ± 0.08 a.u., respectively. From the latter value we obtain the absolute BBR shift as −0.0041 ± 0.0007 Hz which then translates to the relative BBR shift of (−3.66 ± 0.60) × 10⁻¹⁸ for the measured clock frequency of 1.12105393207851 × 10⁻¹⁵ Hz [7]. It is the most accurate estimate of the BBR shift in Al⁺ to date, using which the systematic error of the clock-frequency measurement [7] can be reduced by 28%.

The financial support of M.K. has been provided by the ERC, Grant No. 200639, and by the OTKA, Grant No. NF72194. M.K. and B.P.D. acknowledge the Indo-Hungarian (IND 04/2006) project. M.K. acknowledges the Bolyai Scholarship of the Hungarian Academy of Sciences. B.K.S. thanks T. Rosenband for useful discussions. L.V. has been supported by NWO through the VICI programme.

TABLE III. Comparison of theoretical and experimental polarizabilities (a.u.), and relative BBR shifts.

<table>
<thead>
<tr>
<th>Polarizability</th>
<th>Relative BBR shift (units of 10¹⁵)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s² 3p⁶ 3S⁰_u</td>
<td>3s³p³ 3P⁰_u</td>
<td></td>
</tr>
<tr>
<td>24.19</td>
<td>[13]</td>
<td></td>
</tr>
<tr>
<td>24.20 ± 0.75</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>24.14 ± 0.12</td>
<td>24.62 ± 0.25</td>
<td>4.18 ± 3.18</td>
</tr>
<tr>
<td>24.14 ± 0.08</td>
<td>24.61 ± 0.12</td>
<td>3.66 ± 0.60</td>
</tr>
</tbody>
</table>

[21] MRCC, written by M. Kállay (see [http://www.mrcc.hu]).