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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 Al^{+} clock has been estimated precisely. The computed shift relative to the frequency of the $3s^2\,{}^1S_0^e \rightarrow 3s3p\,{}^3P_0^o$ 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 atomic clocks [1,2], probes of fundamental symmetry violations [3–6], and search for the variation in the fundamental constants [7]. The relativistic coupled-cluster (CC) method with single and double excitations (CCSD) supplemented by the important triple excitations has yielded reasonably accurate results [3–5,8]. However, an extension to this method by including higher excitations and its application to large systems are extremely challenging. The general nonrelativistic CC approach of Kállay and co-workers provides one of the most efficient routes to the incorporation of higher excitations by exploiting the features of the many-body diagrammatic techniques and using automated programming tools based on the strings of spin-orbital labels [9].

In this Rapid Communication, we extend the general-order nonrelativistic CC work [9] to the relativistic framework and we also consider its extension to linear-response (LR) calculations which is the first application of its kind to atoms. The new relativistic CC code has a great potential for high-precision studies in several important areas of fundamental physics; to mention a few: atomic clocks, parity nonconservation, electric dipole moment due to parity, and time reversal violations. As a proof of principle, we have employed the method for the calculation of the black-body radiation (BBR) shift of the $3s^2\,{}^1S_0^e \rightarrow 3s3p\,{}^3P_0^o$ clock transition of Al^{+}. This transition provides the basis for the most accurate atomic clock to date [1,7,10], for which the fractional frequency inaccuracy has recently been estimated as 8.6×10^{-18} [7]. Although the size of the BBR shift in the Al^{+} clock is smaller than those in most of the other ions considered for atomic clocks, the associated uncertainty in the estimated BBR shift is about 35% of the total uncertainty when calculated using static polarizabilities and oscillator strengths taken from different sources [11]. Other semiempirical configuration interaction (CI) calculations [12] and nonrelativistic results [13–15] agree with this estimate.

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

$$|\Psi_{\rm CC}\rangle = e^{\hat{T}}|0\rangle, \tag{1}$$

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

$$\hat{T}_k = \sum_{\substack{a_1<a_2\ldots<a_k\\ i_1<i_2\ldots<i_k}} t_{i_1 i_2 \ldots i_k}^{a_1 a_2 \ldots a_k}\, a_1^{+} i_1^{-} a_2^{+} i_2^{-} \cdots\, a_k^{+} i_k^{-}. \tag{2}$$

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 $|\Psi_{i_1 i_2 \cdots i_k}^{a_1 a_2 \cdots a_k}\rangle = a_1^{+} i_1^{-} a_2^{+} i_2^{-} \cdots a_k^{+} i_k^{-}|0\rangle$ we get the nonlinear algebraic equations for the correlation energy E and unknown cluster amplitudes $t_{i_1 i_2 \cdots i_k}^{a_1 a_2 \cdots a_k}$ for the excitation of any order as

$$\left\langle \Psi_{i_1 i_2 \cdots i_k}^{a_1 a_2 \cdots a_k} \middle| e^{-\hat{T}} \hat{H}_N e^{\hat{T}} \middle| 0 \right\rangle = E\delta_{k,0}, \quad (k = 0, \ldots, n), \tag{3}$$

where $\hat{H}_N$ is the normal-ordered Dirac-Coulomb (DC) Hamiltonian and k is the level of excitation. The CC approaches corresponding 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 ω are calculated by determining the right-hand eigenvalues of the CC Jacobian as

$$\left\langle \Psi_{i_1 i_2 \cdots i_k}^{a_1 a_2 \cdots a_k} \middle| [e^{-\hat{T}} \hat{H}_N e^{\hat{T}}, \hat{R}] \middle| 0 \right\rangle = \omega\, r_{i_1 i_2 \cdots i_k}^{a_1 a_2 \cdots a_k}, \tag{4}$$

where operator $\hat{R}$ has the same structure as the cluster operator with parameters $r_{i_1 i_2 \cdots i_k}^{a_1 a_2 \cdots a_k}$.

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 formalism [18]. 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 at the same level of excitation are known to be more accurate, furthermore the latter are size consistent, which could be important for heavy elements.

As is well known, the energy of the ith state of an atom placed in an isotropic electric field of strength ε changes as

$$E_i(\varepsilon) = E_i(0) - \frac{\alpha_i}{2}\varepsilon^2 - \cdots, \qquad (5)$$

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 α_i is the static dipole polarizability of state i. The BBR shift for a transition $|J_i,M_i\rangle \rightarrow |J_j,M_j\rangle$ 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

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

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 ε. 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 ε were fixed to 1×10^{-3} and 2×10^{-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-ζ 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 $X\zeta$ 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 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,

TABLE I. Calculated excitation energies (cm^{-1}) and polarizabilities (a.u.).

		Polarizability		
Level of correlation	Excitation energy	$3s^2\ {}^1S_0^e$	$3s3p\ {}^3P_0^o$	Differential
Basis: 2ζ ($16s$, $12p$, $5d$ spinors)[a]				
CCSD	37 222	24.215	24.380	0.165
CCSDT	37 324	24.158	24.357	0.199
CCSDTQ	37 326	24.156	24.358	0.202
Basis: 2ζ ($16s$, $12p$, $5d$ spinors)				
CCSD	37 005	24.203	24.261	0.058
CCSDT	37 167	24.072	24.208	0.136
Basis: 3ζ ($20s$, $14p$, $7d$, $5f$ spinors)				
CCSD	37 228	24.143	25.040	0.897
CCSDT	37 373	24.017	24.979	0.962
Basis: 4ζ ($22s$, $17p$, $9d$, $7f$, $5g$ spinors)				
CCSD	37 160	24.273	24.700	0.427
Basis: 5ζ ($23s$, $17p$, $11d$, $9f$, $7g$, $5h$ spinors)				
CCSD	37 186	24.251	24.656	0.406

[a] $1s$, $2s$, and virtual orbitals above $5E_H$ are frozen (here E_H is the Hartree energy).

e.g., Ref. [23]). In this approach any property P, i.e., excitation energy, polarizability, or differential polarizability, is evaluated as

$$P = P_{\mathrm{CCSD}} + \Delta P_{\mathrm{T}} + \Delta P_{\mathrm{Q}} + \Delta P_{\mathrm{BQ}}, \tag{7}$$

where $\Delta P_{\mathrm{T}} = P_{\mathrm{CCSDT}} - P_{\mathrm{CCSD}}$, $\Delta P_{\mathrm{Q}} = P_{\mathrm{CCSDTQ}} - P_{\mathrm{CCSDT}}$, while P_{CCSD}, P_{CCSDT}, and P_{CCSDTQ} are the values calculated for property P using the CCSD, CCSDT, and CCSDTQ methods, respectively. ΔP_{BQ} is the contributions from the Breit interaction and QED corrections. We will simply denote the P_{CCSD}, ΔP_{T}, and ΔP_{Q} values computed with an $X\zeta$ basis set as $P_{\mathrm{CCSD}}|_{X\zeta}$, $\Delta P_{\mathrm{T}}|_{X\zeta}$, and $\Delta P_{\mathrm{Q}}|_{X\zeta}$, 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_{CCSD} and ΔP_{T} were computed with the 5ζ and 3ζ basis sets, respectively, correlating all electrons and all orbitals. The evaluation of ΔP_{Q} was only feasible with the 2ζ basis set, but further approximations were necessary even in this basis, and the $1s$ and $2s$ electrons were frozen as well as the virtual orbitals lying above $5E_H$ were dropped. The ΔP_{BQ} correction was estimated using the numerical multiconfigurational Dirac-Fock (MCDF) method as implemented in the MCDFGME 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 CCSD values themselves are already quite reliable with the contribution of triple excitations to both properties amounting to less than 1%. Although the ΔP_{T} correction to the polarizability shift is only 0.07 a.u., this contribution does still represent more than 10% of the composite shift value and cannot be ignored. The effect of quadruple excitations is approximately two orders of magnitude smaller than that of the triples and can be considered as negligible, which also implies that it is justified to ignore the effect of pentuple and higher excitations.

The basis-set convergence of the properties we have studied follows the usual trend. The polarizabilities and excitation energies are already reliable in the smaller basis sets, while the polarizability shift, which is a small difference of two large numbers, requires larger basis sets. From the comparison of the 4ζ and 5ζ results we observe that the CCSD excitation energies and polarizabilities change on the scales of 10 cm^{-1} and 0.01 a.u., respectively, which means that the relative change is about 0.1% for both properties. Unfortunately the errors of the ground- and excited-state polarizabilities do not cancel each other, and consequently the absolute error of the CCSD polarizability shift is larger. For the aforementioned reason its relative error is also significantly larger, a couple of percent of the total value. Similar conclusions can be drawn for the contribution of triple excitations. The $\Delta P_{\mathrm{T}}|_{X\zeta}$ increment also changes in the 10 cm^{-1} and 0.01 a.u. range for excitation energies and polarizabilities, respectively, when going from $X = 2$ to 3, and the change in the polarizability shift is only 0.013 a.u.

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_{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 $X\zeta$ ($X \geqslant 3$) correlation-consistent basis sets the first contribution converges exponentially to the infinite basis-set limit. This similarly holds for the correlation contribution if $X \leqslant 5$, while its convergence slows down with the larger basis sets. In practice, if P_{CCSD} is evaluated with the $X\zeta$, $(X+1)\zeta$, and $(X+2)\zeta$ basis sets, the $[P_{\mathrm{CCSD}}|_{(X+1)\zeta} - P_{\mathrm{CCSD}}|_{X\zeta}]/[P_{\mathrm{CCSD}}|_{(X+2)\zeta} - P_{\mathrm{CCSD}}|_{(X+1)\zeta}]$ ratio is considerably larger than two if $X = 3$, while it is closer 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 $P_{\mathrm{CCSD}}|_{X\zeta}$ with respect to the hypothetic P_{CCSD} value computed in the infinite basis is identical to $P_{\mathrm{CCSD}}|_{X\zeta} - P_{\mathrm{CCSD}}|_{(X-1)\zeta}$ 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 $P_{\mathrm{CCSD}}|_{4\zeta} - P_{\mathrm{CCSD}}|_{3\zeta}$ and $P_{\mathrm{CCSD}}|_{5\zeta} - P_{\mathrm{CCSD}}|_{4\zeta}$ 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 $P_{\mathrm{CCSD}}|_{5\zeta} - P_{\mathrm{CCSD}}|_{4\zeta}$ difference is a conservative estimate for the basis set error of the $P_{\mathrm{CCSD}}|_{5\zeta}$ values, and we attach these numbers as error bars. The convergence of ΔP_{T} with the basis set is known to be similar to that of the correlation contribution to P_{CCSD} [26]. Therefore we take again $2 \times (\Delta P_{\mathrm{T}}|_{3\zeta} - \Delta P_{\mathrm{T}}|_{2\zeta})$ as a conservative choice for the error. The ΔP_{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 2ζ 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 ΔP_{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 II. Composite excitation energy (cm^{-1}), polarizabilities (a.u.), and their estimated errors.

		Polarizability			
Contribution	Excitation energy	$3s^2\ {}^1S_0^e$	$3s3p\ {}^3P_0^o$	Differential	Source
P_{CCSD}	37186 ± 52	24.251 ± 0.044	24.656 ± 0.088	0.406 ± 0.042	5ζ basis set
ΔP_{T}	146 ± 33	-0.126 ± 0.011	-0.061 ± 0.015	0.065 ± 0.026	3ζ basis set
ΔP_{Q}	2 ± 4	-0.002 ± 0.005	0.001 ± 0.002	0.003 ± 0.007	2ζ basis set
ΔP_{BQ}	-6 ± 6	0.015 ± 0.015	0.018 ± 0.018	0.003 ± 0.003	Numerical MCDF
Composite	37326 ± 95	24.137 ± 0.075	24.614 ± 0.123	0.477 ± 0.078	Sum of all contributions

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

Polarizability		Relative BBR shift	
$3s^2\ ^1S_0^e$	$3s3p\ ^3P_0^o$	(units of 10^{18})	Reference
24.19			[13]
24.83 ± 5.26	24.63 ± 4.93	-8 ± 3	[11]
24.20 ± 0.75			[14]
24.14 ± 0.12	24.62 ± 0.25	-4.18 ± 3.18	[12]
24.14 ± 0.08	24.61 ± 0.12	-3.66 ± 0.60	This work

incompleteness errors. As the missing correlation contribution to this correction is not expected to exceed its MCDF 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 $(-3.66 \pm 0.60) \times 10^{-18}$ for the measured clock frequency of $1.121015393207851 \times 10^{-15}$ 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%.

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