

Recovery and Resilience Plan of the Slovak Republic.**09I03-03-V04 Fellowship for excellent researchers****Development of accurate relativistic coupled cluster methods for simulating atomic clocks****Project number - 09I03-03-V04-00117***A protocol for simulating blackbody radiation shift in atomic clock candidates.***PROJECT AND DELIVERABLE INFORMATION SHEET**

Project: Development of accurate relativistic coupled cluster methods for simulating atomic clocks	Grant agreement number	09I03-03-V04-00117
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	Deliverable title	A protocol for simulating blackbody radiation shift in atomic clock candidates
	Deliverable nature/description	It contains the protocol for the calculation of transition energies corresponding to the clock transition in atomic clock candidates, together with the corresponding ground and excited state static polarizabilities using a finite-field approach. The calculated values have been benchmarked against theoretical and experimental results available in the literature for the worked example (the Sr atom). The effect of the basis set, the level of correlation, the inner-core correlation and the higher-order relativistic effects on the calculated relativistic CCSDT and EOM-CCSDT results has been investigated. The blackbody radiation (BBR) shift has been estimated from the static polarizability difference between the two states involved in the transition, together with a systematic error budget.
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Created by	Achintya Kumar Dutta
Contributors	Ján Šimunek
Reviewed by	Jozef Noga

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1. Scope and intent of the protocol

This document describes the protocol developed within the DAREMAC project (09I03-03-V04-00117) for the ab initio simulation of the blackbody-radiation (BBR) shift on the clock transition of optical-atomic-clock candidates. The protocol is the deliverable D3.1 of work package W3 (Simulation of atomic clock candidates) and rests on the lower-scaling relativistic equation-of-motion coupled-cluster (EOM-CC) infrastructure delivered in deliverables D1.1 (ground state CCSDT) and D2.1 (excited state EOM-CCSDT with state-specific frozen natural spinor and CD-X2CAMF acceleration).

The protocol is method-prescriptive: it lists, in the order they must be executed, the calculations needed to obtain a recommended value of the BBR shift on a clock transition together with a defensible systematic uncertainty budget. It is designed to be applicable to any neutral atom or ion considered as a candidate for an optical lattice clock or an ion-trap clock, subject to the limitations discussed in Section 5. The Sr atom is used throughout as the worked example, since it is currently the most extensively documented optical-clock species and provides both experimental anchors and independent theoretical points of comparison.

The protocol has been validated within the DAREMAC project on the $1S0 \rightarrow 3P0$ clock transition of Sr using the BAGH codes, the results were cross verified using an independent atomic spherical-symmetry RCC code. The full set of underlying calculations and their cross-validation is reported in the accompanying manuscript (Chamoli, Chakraborty, Sahoo, Šimunek, Noga, Dutta, in preparation), which is also annexed as deliverable D4.x for this project.

2. Theoretical foundations

2.1 The blackbody radiation shift

The thermal fluctuations of the electromagnetic field surrounding a trapped atom or ion give rise, through the AC Stark effect, to a temperature-dependent shift of the atomic energy levels. The resulting frequency shift on a clock transition between states i and j is, in the standard approximation,

$$\delta E = -\frac{1}{2}(831.9 \text{ V/m})^2 \left(\frac{T}{300}\right)^4 (\alpha_i^0 - \alpha_j^0) (1 + \eta)$$

where α_i^0 and α_j^0 are the static scalar electric-dipole polarizabilities of the two states, $T = 300 \text{ K}$ is the standard temperature, and η is a small dynamic correction reflecting the frequency distribution of the BBR field. For the typical clock candidates considered within DAREMAC, η is below 10^{-3} and is omitted in the present protocol (see Step 11). The accuracy of the calculated BBR shift is therefore controlled entirely by the accuracy of the differential static polarizability $\Delta\alpha = \alpha(\text{excited}) - \alpha(\text{ground})$.

2.2 Static dipole polarizability

The static scalar polarizability of a stationary state of an atom in a weak homogeneous electric field of magnitude F can be obtained as the second derivative of the energy with respect to the field strength,

$$\alpha = - \left(\frac{\delta^2 E(|F|)}{\delta |F| \delta |F|} \right)_{|F|=0}$$

or, equivalently, as the zero-frequency limit of the linear-response function for the dipole operator. We have used the finite field approach in this protocol, where the dipole-perturbed Hamiltonian $H = H_0 - F \cdot D$ is solved at several small field strengths, and α is calculated through three- or five-point numerical differentiation. The FF approach extends naturally to both ground and excited states (the latter through state-selected EOM-CC energies) and is trivially parallel across field strengths. The analytic linear-response (LR) approach, in which α is obtained from the perturbed coupled-cluster t and Λ amplitudes evaluated at zero frequency; it is exact within the CC truncation and avoids any numerical-differentiation noise. Within the protocol, the LR approach is used as a cross-check on the ground-state FF polarizability.

2.3 Relativistic coupled cluster method for ground and excited states

For an atomic clock candidate, the wave function in the four-component Dirac–Hartree–Fock (DHF) reference is written as $|\Psi_{CC}\rangle = \exp(\hat{T})|\Phi_0\rangle$, where the cluster operator $\hat{T}$ generates particle–hole excitations from the DHF determinant. Truncation at the singles-and-doubles level yields the relativistic CCSD method; full inclusion of three-body operators gives CCSDT. Excited states are accessed through the equation-of-motion construction $|\Psi_k\rangle = \hat{R}_k \exp(\hat{T})|\Phi_0\rangle$, with $\hat{R}_k$ truncated at the singles and doubles (EOM-CCSD), or at the singles, doubles, and triples (EOM-CCSDT) level. Within the DAREMAC implementation, the canonical relativistic EOM-CCSDT method scales as $O(N^8)$ iteratively with $O(N^6)$ storage; the lower-scaling state-specific frozen-natural-spinor variant combined with the CD-X2CAMF Hamiltonian and the EOM-CCSD(T)(a)* perturbative-triples correction reduces this to non-iterative $O(N^7)$ at storage comparable to EOM-CCSD (see D1.1 and D2.1). Both implementations are used in the protocol below.

3. The protocol

The twelve steps of the protocol are executed in the order presented. Steps 1–3 are setup; Steps 4–8 produce the individual contributions to the composite polarizability; Steps 9–11 assemble the final BBR shift and its uncertainty budget. Where parameter choices are recommended (basis-set families, field strengths, FNS thresholds, etc.) the recommendation is based on the convergence tests carried out in D1.1, D2.1, and the worked example reported in Section 4.

Step 1. Choice of Hamiltonian

Adopt the four-component Dirac–Coulomb (DC) Hamiltonian as the baseline, including the no-pair approximation (positive-energy projection) for the correlation treatment. Higher-order relativistic effects such as the Gaunt and Breit interactions are introduced only as additive

corrections at the DHF level in Step 8. For systems with a maximum atomic number $Z \leq 60$ the spin-free X2C Hamiltonian combined with the atomic mean-field (X2CAMF) treatment of spin-orbit coupling is acceptable as the baseline and reduces the integral cost dramatically, as demonstrated in D2.1; for heavier candidates ($Z > 60$) the full 4c-DC Hamiltonian is mandatory for the baseline and the X2CAMF approximation may be used only for higher basis sets.

Step 2. Choice of one-electron basis set and CBS extrapolation

Use the uncontracted doubly-augmented dyall.aeXZ family of all-electron basis sets with $X = 2, 3, 4$ in sequence. For each clock candidate, the polarizability and the clock transition energy are computed at d-aug-dyall.ae2z, d-aug-dyall.ae3z, and d-aug-dyall.ae4z. **Diffuse functions are critical:** the excited-state polarizability of an alkaline-earth-metal clock state can change by tens of a.u. between singly and doubly augmented basis sets, and the protocol mandates at least double augmentation. The complete-basis-set (CBS) limit is obtained by extrapolation. Four extrapolation schemes (Martin; Feller + Helgaker; Feller + Lesiuk; Peterson + Dunning) are computed in parallel. The Martin scheme is taken as the recommended value; the spread across the four schemes is folded into the uncertainty budget in Step 12. For the basis-set incompleteness error half of the spread of the four schemes is adopted as the uncertainty contribution.

Step 3. Reference state and frozen-core scheme

The reference determinant is obtained from a converged Dirac–Hartree–Fock calculation in the chosen basis. The frozen-core approximation is applied to all production polarizability calculations: the innermost core electrons (typically those not chemically active in the clock transition; e.g. 18 electrons for Sr, 28 for Yb-like systems) are excluded from the correlation treatment. The core-correlation contribution is then recovered as the Δ_{core} additive correction in Step 7 to keep the computational cost manageable for the triples-level steps.

Step 4. Ground-state polarizability (finite field)

Perform single-point relativistic CCSD calculations on the ground state in the presence of a homogeneous electric field along the z axis at the field strengths $|F| \in \{+0.001, -0.001, +0.0005, -0.0005, 0\}$ atomic units, in the chosen basis set. The static dipole polarizability is then obtained from the central-difference expression

$$\alpha = - [E(+F) + E(-F) - 2 E(0)] / F^2$$

evaluated at $F = 0.001$ a.u., which has been verified in the worked example to be the optimal compromise between truncation error (favouring small F) and numerical noise (favouring large F). Repeat the calculation at d-aug-dyall.ae2z, ae3z, and ae4z; the CBS-extrapolated CCSD ground-state polarizability is the baseline $\alpha^0_{\text{ground}}(\text{CCSD/CBS})$ entering Step 9.

As an internal consistency check, the analytic linear-response CCSD polarizability is also computed at d-aug-dyall.ae2z. The FF and LR values must agree to within ~ 0.1 a.u.; a larger

discrepancy indicates a numerical-differentiation problem (Step 12 sets the numerical-noise uncertainty).

Step 5. Excited-state polarizability (finite field, EOM-CCSDT)

For each excited state involved in the clock transition (including all relevant $|M_J|$ sublevels in the case of multiplet states), perform the corresponding EOM-CCSD calculation at the five field strengths of Step 4 and extract α via the same central-difference expression. For excited states whose wave function has significant Rydberg or diffuse character (e.g. ^3P states of alkaline-earth metals), the polarizability converges much more slowly with basis-set size than the ground-state polarizability, and CBS extrapolation across three cardinal numbers is mandatory. The same four CBS schemes used in Step 2 are applied. The CBS-extrapolated EOM-CCSD excited-state polarizability is the baseline $\alpha^0_{\text{excited}}(\text{EOM-CCSD/CBS})$ entering Step 9.

Within EOM-CC, the M_J -dependence of the excited-state polarizability of a multiplet must be resolved separately: each $|M_J|$ sublevel of a $J \geq 1$ state has its own α value, and the scalar polarizability relevant for the BBR shift is the $(2J+1)$ -weighted average. The protocol therefore requires that all $|M_J|$ sublevels of the excited state be computed individually, never collapsed to a single root.

Step 6. Correlation corrections beyond CCSD

Two triples-correction strategies are run independently, and their difference is used as an estimate of the triples-correction reliability in Step 11. **(a)** The full iterative ΔT correction, $\Delta T = \alpha(\text{CCSDT}) - \alpha(\text{CCSD})$, is computed at the s-aug-dyall.ae2z basis set, using the canonical relativistic CCSDT and EOM-CCSDT implementation of W1 and W2. **(b)** The perturbative $\Delta(T)$ correction, $\Delta(T) = \alpha(\text{CCSD}(T)(a)^*) - \alpha(\text{CCSD})$, is computed at the same s-aug-dyall.ae2z basis set, using the lower-scaling SS-FNS-EOM-CCSD(T)(a)* implementation of D2.1. The ΔT correction from the full CCSDT calculation is adopted in the composite assembly of Step 10; $\Delta(T)$ is retained for diagnostic purposes only, and $|\Delta T - \Delta(T)|$ enters the uncertainty budget. An additional conservative allowance for higher-order excitations (quadruples and beyond) is set at 0.5 a.u. for the ground-state polarizability, 1.0 a.u. for the excited-state polarizability, and 10 cm^{-1} for the clock transition energy unless a different value is supported by direct CCSDTQ data on a representative reference system.

Step 7. Inner-core correlation correction (Δ_{core})

At the d-aug-dyall.ae2z level, perform two CCSD (and EOM-CCSD for the excited state) calculations: one with the standard frozen-core scheme of Step 3, and one in which all electrons of the system are correlated. The difference $\alpha(\text{all-electron}) - \alpha(\text{frozen-core})$ at the d-aug-dyall.ae2z level is the Δ_{core} correction. Half of $|\Delta_{\text{core}}|$ is taken as the corresponding uncertainty in Step 11.

Step 8. Higher-order relativistic correction (Δ_{Gaunt})

At the d-aug-dyall.ae2z level, perform two DHF + CCSD/EOM-CCSD calculations: one with the pure DC Hamiltonian (Step 1 baseline) and one with the Hamiltonian augmented by the Gaunt operator, defined as

$$G_{ij} = -\alpha_i \cdot \alpha_j / (2 r_{ij})$$

at the DHF stage only. The difference between the two calculations defines ΔGaunt . The Breit retardation contribution is verified at the same level and confirmed to be negligible for all clock candidates considered to date; it is folded into the relativistic-effect uncertainty (half of $|\Delta\text{Gaunt}|$) in Step 11.

Step 9. Composite polarizability assembly

The recommended composite polarizability for each clock state is assembled as

$$\alpha^0_{\text{composite}} = \alpha(\text{CCSD/CBS}) + \Delta T + \Delta\text{core} + \Delta\text{Gaunt}$$

with the ΔT contribution taken from the full iterative CCSDT calculation of Step 6 (the perturbative $\Delta(T)$ is not added; it is used only for the uncertainty estimate in Step 11). The composite excitation energy is assembled in the same way:

$$\omega_{\text{composite}} = \omega(\text{CCSD/CBS}) + \Delta T_{\omega} + \Delta\text{core}_{\omega} + \Delta\text{Gaunt}_{\omega}$$

where each correction is the corresponding shift in the transition energy obtained from the two calculations defining that correction.

Step 10. BBR-shift evaluation

With the composite polarizabilities of the two clock states in hand, the BBR shift at $T = 300$ K is evaluated from Eq. (2.1):

$$\delta v_{\text{BBR}} = -\frac{1}{2} (831.9 \text{ V/m})^2 [\alpha^0_{\text{excited}} - \alpha^0_{\text{ground}}] \text{ (in atomic units, converted to Hz)}$$

The dynamic-correction factor η is set to zero by default; for systems where $|\eta| > 10^{-3}$ is suspected (e.g. clock candidates with low-lying excited states close in energy to the upper clock state) the multipolar treatment of Porsev and Derevianko [Phys. Rev. A 74, 020502R (2006)] is used to evaluate η explicitly. The differential polarizability $\Delta\alpha = \alpha(\text{excited}) - \alpha(\text{ground})$ is reported alongside δv_{BBR} and the fractional shift $\delta v/v_0$, where v_0 is the unperturbed clock frequency obtained from Step 5.

Step 11. Systematic error budget

The total uncertainty on the composite polarizability is obtained as the root-sum-square of six independent contributions. For each contribution, half of the absolute value of the corresponding correction or spread is taken as the 1σ uncertainty. The six contributions are listed below; the values quoted in parentheses are illustrative orders of magnitude observed in the Sr worked example (Section 4), to be re-evaluated for each new clock candidate.

Uncertainty source	Estimation rule
Triples correction (ΔT vs $\Delta(T)$ spread)	$ \Delta T - \Delta(T) $ from Step 6, evaluated at the s-aug-dyall.ae2z level.
Missing higher-order correlation (Q and beyond)	Conservative allowance from Step 6: 0.5 a.u. (ground), 1.0 a.u. (excited), 10 cm ⁻¹ (transition).
Basis-set incompleteness (CBS spread)	Half of the spread across the four CBS extrapolation schemes from Step 2.
Inner-core correlation (Δ_{core} reliability)	Half of $ \Delta_{\text{core}} $ from Step 7.
Higher-order relativistic effects	Half of $ \Delta_{\text{Gaunt}} $ from Step 8, plus the Breit retardation contribution where it exceeds 10% of Δ_{Gaunt} .
Numerical noise of finite differentiation	Difference of α evaluated at $F = 0.001$ a.u. and $F = 0.0001$ a.u. from Step 4.

The contributions are combined in quadrature to give the 1σ uncertainty on the composite polarizability of each state. The uncertainty on $\Delta\alpha$ is obtained by propagating the individual state uncertainties through their (uncorrelated) sum, which is the conservative assumption.

4. Worked example: the Sr clock $1S_0 \rightarrow 3P_0$ transition

The protocol has been executed on the Sr atom, currently one of the most thoroughly characterised optical lattice-clock species. The clock transition is $5s^2 \ ^1S_0 \rightarrow 5s5p \ ^3P_0$ at $\omega_0 \approx 14\,317 \text{ cm}^{-1}$ (experimental).

Basis set	$\alpha(^1S_0)$ [a.u.]	$\alpha(^3P_0)$ [a.u.]	ω_0 [cm ⁻¹]
d-aug-dyall.ae2z	203.26	344.79	14176
d-aug-dyall.ae3z	203.01	418.62	14193
d-aug-dyall.ae4z	202.45	434.84	14199
CBS (Martin)	201.67	443.36	14205
Experiment	186(15)	—	14317

Table 4.1. Sr ground- and excited-state polarizabilities and clock transition energy at the relativistic EOM-CCSD level (Step 5), as a function of basis set, with the Martin CBS extrapolation (Step 2).

The full set of underlying calculations is reported in the accompanying manuscript (Chamoli, Chakraborty, Sahoo, Šimunek, Noga, Dutta, in preparation); the headline numbers, organised by the steps above, are reproduced here as the worked example.

Table 4.1 illustrates the typical convergence pattern: the ground-state polarizability is essentially converged at double-zeta (a 1.6 a.u. spread from ae2z to CBS), whereas the excited-state polarizability moves by almost 100 a.u. across the same range. The clock transition energy converges to within 6 cm⁻¹ of the CBS limit at quadruple-zeta.

Contribution	$\alpha(^1S_0)$ [a.u.]	$\alpha(^3P_0)$ [a.u.]	ω_0 [cm ⁻¹]
CCSD/CBS	201.67	443.36	14205
+ ΔT (Step 6, CCSDT)	-3.45	+0.65	+1
+ Δ_{core} (Step 7)	-0.02	+1.42	-17
+ Δ_{Gaunt} (Step 8)	+0.04	+1.43	+13
Composite (Step 10)	198.24	446.86	14202
Composite uncertainty	± 2.12	± 7.93	± 53
Experiment	186(15)	—	14317

Table 4.2. Step-by-step assembly of the composite polarizability and clock transition energy of the $\text{Sr } ^1S_0 \rightarrow ^3P_0$ transition. The ΔT correction is from full iterative EOM-CCSDT (Step 6, full-triples branch); the perturbative $\Delta(T)$ correction is used only for the uncertainty in Step 11 and is therefore not added.

Cross-validation against the independent atomic-code calculation (Step 9) yields a ground-state polarizability of 195(5) a.u. via the perturbed-RCC method in spherical symmetry; this is consistent with the molecular-code EOM-CC composite value of 198.24 ± 2.12 a.u. within their respective uncertainties and lies well within the experimental error bar of 186 ± 15 a.u. (Schwartz, Miller, and Bederson, 1974). The agreement between the molecular FF-DHF and atomic RPA values (~ 232.6 a.u. in both implementations) confirms the consistency of the finite-field and perturbative implementations across the two independent codes.

Transition	$\delta\nu$ [Hz]	ν_0 [Hz]	$\delta\nu/\nu_0$
$^1S_0 \rightarrow ^3P_0$ (this protocol)	-2.32 ± 0.09	4.29×10^{14}	$(-5.40 \pm 0.21) \times 10^{-15}$
$^1S_0 \rightarrow ^3P_0$ (Lisdat et al. 2021)	-2.354 ± 0.032	4.29×10^{14}	-5.5×10^{-15}

Transition	$\delta\nu$ [Hz]	ν_0 [Hz]	$\delta\nu/\nu_0$
$^1S_0 \rightarrow ^3P_1$ ($ MJ =1$, this work)	-2.84	4.33×10^{14}	-6.52×10^{-15}
$^1S_0 \rightarrow ^3P_2$ ($ MJ =0$, this work)	-3.24	4.45×10^{14}	-7.25×10^{-15}

Table 4.3. BBR shift of the Sr clock $1S_0 \rightarrow 3P_0$ transition at $T = 300$ K from Step 11, together with the BBR shifts of the related $1S_0 \rightarrow 3P_1$ ($|MJ|=1$) and $1S_0 \rightarrow 3P_2$ ($|MJ|=0$) transitions. The Lisdat et al. (2021) value is shown for comparison.

The protocol therefore reproduces, with a defensible error budget, the most recent experimental BBR-shift reference value for the Sr clock transition, while providing previously unreported predictions for the related $^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^3P_2$ transitions. This serves as the protocol's validation for the deliverable D3.1.

5. Applicability and limitations

The protocol is directly applicable, without modification, to any neutral atom or singly charged ion considered as a candidate for an optical lattice clock or an ion-trap clock, provided the clock transition is dominated by single excitations on top of a closed-shell or essentially closed-shell reference. The Sr, Yb, Hg, and Cd atomic-clock candidates and the Al^+ , In^+ , Sr^+ , and Lu^+ ion-clock candidates all fall within this regime.

Three classes of system fall outside the scope of the present protocol and require methodology extensions that are deferred to follow-up work.

(i) *Strongly multireference clock candidates* (open-shell systems with near-degeneracy of low-lying electronic states, transition-metal ions). The single-reference EOM-CC framework can suffer convergence problems; a multireference Fock-space CC treatment, available within the host group's THEOCHEM expertise but not yet integrated with the SS-FNS + CD-X2CAMF infrastructure of D1.1 and D2.1, would be required.

(ii) *Highly-charged-ion clock candidates*: The four-component DC Hamiltonian remains adequate, but the contribution from QED corrections, self-energy and vacuum polarization beyond the leading-order Uehling potential becomes non-negligible at the precision targeted by next-generation clocks; the present protocol provides $\Delta Gaunt$ and the leading vacuum-polarization correction but does not include higher-order QED.

(iii) *Molecular clock candidates* (e.g. diatomic molecular ions for tests of fundamental physics). The protocol structure carries over essentially unchanged, but vibrational and rotational averaging of the polarizability over the molecular state must be added, and the symmetry-adaptation of the polarizability tensor differs from the atomic case (parallel and perpendicular components must be tracked separately). The accompanying manuscript of the worked example focuses on the atomic

case; an extension of the protocol to small clock molecules is a natural follow-up to DAREMAC and is anticipated in Section 1.1 of the original project proposal.

Finally, the protocol estimates the BBR shift at the standard temperature $T = 300$ K. The temperature dependence of the BBR shift is captured by the explicit T^4 scaling of Eq. (2.1) provided that $\eta \ll 1$; for clock candidates with low-lying excited states close in energy to the upper clock state, the multipolar dynamic correction must be evaluated explicitly and added to the protocol output as a separate contribution.

6. References

The protocol uses the methodology developed in deliverables D1.1, D2.1, and D4.5–D4.7 of the present project (cited in those deliverables and in the conclusion of D2.1) and synthesises the existing literature on BBR-shift calculations. The principal external references are:

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