

Multipole blackbody radiation shift of Rydberg energy levels

R. M. Potvliege 

Department of Physics, [Durham University](#), Durham DH1 3LE, England, United Kingdom



(Received 10 June 2026; accepted 28 August 2026; published 14 September 2026)

We study the role of retardation in the energy shift of Rydberg states induced by thermal radiation, focusing on the case of temperatures higher than those for which the electric dipole approximation is expected to apply. As anticipated by Farley and Wing [J. W. Farley and W. H. Wing, *Phys. Rev. A* **23**, 2397 (1981)], retardation needs to be taken into account in calculations of this energy shift around and above the temperature $\alpha mc^2/(3k_B n^2)$, where n is the principal quantum number of the state considered, m is the mass of the electron, and k_B is the Boltzmann constant, e.g., around and above 1440 K for $n = 100$. The corresponding nondipole shift dominates the electric dipole shift at about 2.5 times that characteristic temperature. Thermal shifts arising from retardation and from the electric quadrupole interaction are of the same order of magnitude as the diamagnetic thermal shift and would thus need to be taken into account in the circumstances where the latter is relevant.

DOI: [10.1103/8s3y-pqbd](#)

I. INTRODUCTION

Quantifying the ac Stark shift induced by the blackbody radiation (BBR) is often important in high-precision spectroscopy and related areas. In particular, the requirements of modern atomic clocks may make it necessary to calculate the BBR shift beyond the electric dipole approximation [1–4]. The current requirements of Rydberg states spectroscopy are less stringent. An estimate of the BBR shift based on the dipole approximation, thus neglecting retardation, normally suffices in this area. How the BBR shift of Rydberg states varies within this approximation has been known for some time, in particular since the publication of a detailed study of the issue by Farley and Wing [5] (some of the numerical results of Ref. [5] have recently been revisited [6]). In the present work, we focus on how this shift varies when this approximation breaks down, a question which does not seem to have been investigated in much detail so far.

The validity of neglecting retardation and multipole couplings when calculating the BBR shift of Rydberg states depends on the temperature and on the states. Farley and Wing [5] noted that the dipole approximation should be expected to break down at temperatures such that the BBR field largely consists of spectral components varying significantly on the length scale of the state considered. This length scale can be taken to be the Bohr radius of the atom, i.e., $r_a = n_a^2$ for a state of principal quantum number n_a (we use Hartree atomic units here and throughout this article, except where specified otherwise). Farley and Wing reckoned that retardation and

multipole interactions may be expected to be significant at temperatures approaching or exceeding the state-dependent temperature T_a at which $k_{\max} r_a = 1$, where $k_{\max}$ is the wave number at which the BBR spectral density is a maximum:

$$T_a = \frac{c}{3n_a^2 k_B}, \quad (1)$$

where k_B denotes the Boltzmann constant. E.g., $T_a = 5770$ K for $n_a = 50$, $T_a = 301$ K for $n_a = 219$, and $T_a = 160$ K for $n_a = 300$. This argument suggests that retardation significantly affects the BBR shift only at temperatures at which population redistribution by the BBR field [5] and (possibly) BBR-induced ionization [7,8] are important.

All high Rydberg states have approximately the same BBR energy shift of $\pi(k_B T)^2/(3c^3)$ within the dipole approximation [5,9]. Namely, denoting the electric dipole shift of state a by $\delta E_a^{(E1)}$,

$$\delta E_a^{(E1)} \sim \frac{\pi}{3} \frac{(k_B T)^2}{c^3} \quad (2)$$

for $n_a \rightarrow \infty$. This asymptotic energy shift amounts to a frequency shift of 2417 Hz at $T = 300$ K. However, it has recently been pointed out that the BBR shift of Rydberg states also includes a contribution from the diamagnetic part of the interaction Hamiltonian and that this contribution may be significant for high enough principal quantum numbers and high enough temperatures [10,11]. Ignoring retardation and relativistic corrections, the diamagnetic energy shift of a state $|a\rangle$ of a single active electron species is

$$\delta E_a^{(D)} = \frac{\pi^3}{45} \frac{(k_B T)^4}{c^5} \langle a | r^2 | a \rangle, \quad (3)$$

where r denotes the distance of the active electron to the nucleus. For a state of hydrogen with principal quantum number n_a and orbital angular momentum quantum number l_a [10,12],

$$\langle a | r^2 | a \rangle = \frac{1}{2} n_a^2 [5n_a^2 - 3l_a(l_a + 1) + 1]. \quad (4)$$

*Contact author: r.m.potvliege@durham.ac.uk

This energy shift translates into a frequency shift $\delta\nu_a^{(D)}$ equal to $\delta E_a^{(D)}/h$, where h is the Planck constant. It amounts to about 1 Hz for the 50s state of hydrogen at room temperature. While small for that state compared to the 2.4-kHz electric dipole shift at the same temperature, $\delta E_a^{(D)}$ increases rapidly with n_a and may therefore contribute significantly to the energy difference between high Rydberg states, at least at sufficiently high temperatures [10].

However, $\delta E_a^{(D)}$ is not the only contribution of order $(k_B T)^4/c^5$ to the BBR shift. We show that in good approximation, the BBR shift takes up the following form for a Rydberg state $|a\rangle$ (this equation does not apply for low-lying states):

$$\delta E_a \approx \delta E_a^{(E1)} + \frac{8\pi^3}{135} \frac{(k_B T)^4}{c^5} \langle a|r^2|a\rangle - \frac{44\pi^5}{42525} \frac{(k_B T)^6}{c^7} \langle a|r^4|a\rangle + \dots \quad (5)$$

The right-hand side is an asymptotic series which rapidly diverges when $T \gtrsim T_a$ but can nonetheless be summed. Its first term is the shift calculated within the dipole approximation. The next term is contributed by the diamagnetic shift $\delta E_a^{(D)}$, by the electric quadrupole term in the multipole expansion of the BBR shift, and by a retardation correction. The higher-order terms are contributed by higher electric multipole shifts and other retardation corrections, including corrections to the diamagnetic shift. Highly precise calculations of the BBR shift would require adding relativistic corrections of relative order $1/c^2$ to each of its terms as well as further corrections, also of relative order $1/c^2$, arising from the paramagnetic part of the interaction Hamiltonian. As explained below, the error introduced by neglecting the relativistic corrections and the paramagnetic shift is negligible in the present context.

Equation (5) is obtained within a further approximation, which is to assume that the sum over intermediate states involved in the calculation of the electric multipole shift of state $|a\rangle$ is dominated by the contributions of states close in energy to $|a\rangle$. We show, in Sec. II, that this approximation is sound for the states and temperatures of interest here. Equation (5) can thus be used for characterizing the behavior of the BBR shift for Rydberg states and temperatures for which the dipole approximation is questionable. It can also be used for estimating the error incurred by approximating the BBR shift by the electric dipole shift $\delta E_a^{(E1)}$.

Calculating the BBR shift with full allowance for retardation, as we do below, makes it possible to address the high-temperature regime where T approaches or exceeds the characteristic temperature T_a of Eq. (1). We show that the BBR shift becomes dominated by nondipole corrections at $T \approx 2.5 T_a$.

The rest of this article is organized in two main sections: we discuss the calculation of the electric multipole shift without retardation in Sec. II, and move to the formulation and calculation of the nonrelativistic BBR shift with retardation in Sec. III. The main body of the paper ends with brief conclusions, in Sec. IV. We only consider the case of an isotropic BBR field. As already mentioned, we generally use Hartree atomic units, except where specified otherwise. We thus equate c with the inverse of the fine-structure constant,

measure lengths in units of the Bohr radius, set $4\pi\epsilon_0$ to 1, and express all energies in hartrees.

II. BBR SHIFT WITHOUT RETARDATION

A. Nonrelativistic theory

We consider a particular Rydberg state of the atom of interest, state $|a\rangle$ say, and the BBR energy shift of this state, δE_a . Ignoring retardation for the time being, we write δE_a as a sum of electric multipole shifts $\delta E_a^{(EK)}$, magnetic multipole shifts $\delta E_a^{(MK)}$, and the diamagnetic shift defined by Eq. (3):

$$\delta E_a = \sum_{K=1}^{\infty} \delta E_a^{(EK)} + \sum_{K=1}^{\infty} \delta E_a^{(MK)} + \delta E_a^{(D)}. \quad (6)$$

Following Ref. [1],

$$\delta E_a^{(EK)} = -\frac{(k_B T/c)^{2K+1}}{2j_a + 1} \sum_p |\langle a||Q_K||p\rangle|^2 F_K\left(\frac{E_p - E_a}{k_B T}\right), \quad (7)$$

where $\{|p\rangle\}$ is a complete set of eigenstates of the field-free Hamiltonian, E_a is the energy of state $|a\rangle$, E_p is the energy of state $|p\rangle$, T is the temperature, Q_K is the electric multipole operator of order K , and

$$F_K(y) = \frac{1}{\pi} \frac{K+1}{K(2K+1)!!(2K-1)!!} \times \text{P.V.} \int_0^\infty \left(\frac{1}{y+x} + \frac{1}{y-x} \right) \frac{x^{2K+1}}{\exp(x)-1} dx. \quad (8)$$

The symbol P.V. indicates that the principal value of the integral is to be used in the calculation. We will assume that each of the intermediate states $|p\rangle$ is characterized by a principal quantum number n_p (or by a wave number k_p for the continuum states), an orbital angular momentum quantum number l_p , and a total angular momentum quantum number j_p . Likewise, state $|a\rangle$ is characterized by the principal quantum number n_a , the orbital angular momentum quantum number l_a , and the total angular momentum quantum number j_a . Then, in terms of the radial matrix elements $\langle a|r^K|p\rangle$,

$$|\langle a||Q_K||p\rangle|^2 = (2j_a + 1)(2j_p + 1)(2l_a + 1)(2l_p + 1) \times \begin{Bmatrix} l_a & l_p & K \\ j_p & j_a & 1/2 \end{Bmatrix}^2 \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 \times |\langle a|r^K|p\rangle|^2. \quad (9)$$

We also assume that a single-active-electron model of the atom is sufficiently accurate for the states of interest, in which case

$$\langle a|r^K|p\rangle = \int_0^\infty R_a^*(r) r^K R_p(r) r^2 dr, \quad (10)$$

where $R_a(r)$ and $R_p(r)$ are the radial wave functions of the respective states.

The summation over j_p implied by Eq. (7) is straightforward in the approximation where E_p and $R_p(r)$ are the same for all the components of a same fine-structure manifold,

since [13]

$$\sum_{j_p} (2j_p + 1)(2l_a + 1) \begin{Bmatrix} l_a & l_p & K \\ j_p & j_a & 1/2 \end{Bmatrix}^2 = 1. \quad (11)$$

In this nonrelativistic approximation,

$$\begin{aligned} \delta E_a^{(EK)} = & - \left(\frac{k_B T}{c} \right)^{2K+1} \sum_{n_p l_p} (2l_p + 1) \\ & \times \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 |\langle n_a l_a | r^K | n_p l_p \rangle|^2 F_K \left(\frac{E_p - E_a}{k_B T} \right). \end{aligned} \quad (12)$$

The electric dipole shift $\delta E_a^{(E1)}$ has been studied by Farley and Wing [5]. We discuss the electric quadrupole shift in Secs. II B 3 and II B 4 and the higher electric multipole shifts in Sec. II B 5. We revisit these results in Sec. III, then with retardation taken into account.

The function $F_K(y)$ takes on a much simpler form when $|y| \ll 1$: for $|y| \rightarrow 0$,

$$F_K(y) \sim -\frac{2y}{\pi} \frac{(K+1)(2K-1)!}{K(2K+1)!!(2K-1)!!} \zeta(2K) \quad (13)$$

where $\zeta(\cdot)$ is the Riemann zeta function [14]. Of particular interest in the following are the energy shifts $\delta E_a^{(EK)^\nu}$, which are defined in the same way as the shifts $\delta E_a^{(EK)}$ but with the function $F_K(y)$ replaced by its small- $|y|$ form:

$$\begin{aligned} \delta E_a^{(EK)^\nu} = & \frac{1}{\pi} \frac{(K+1)(2K-1)!}{K(2K+1)!!(2K-1)!!} \frac{(k_B T)^{2K}}{c^{2K+1}} \\ & \times \frac{2}{2j_a + 1} \sum_p (E_p - E_a) |\langle a || Q_K || p \rangle|^2. \end{aligned} \quad (14)$$

In the nonrelativistic approximation of Eq. (12),

$$\begin{aligned} \delta E_a^{(EK)^\nu} = & \frac{2}{\pi} \frac{(K+1)(2K-1)!}{K(2K+1)!!(2K-1)!!} \frac{(k_B T)^{2K}}{c^{2K+1}} \\ & \times \sum_{n_p l_p} (2l_p + 1) \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 (E_p - E_a) \\ & \times |\langle n_a l_a | r^K | n_p l_p \rangle|^2. \end{aligned} \quad (15)$$

The relevance of the shifts $\delta E_a^{(EK)^\nu}$ stems from the fact that for Rydberg states the shifts $\delta E_a^{(EK)}$ are dominated by the contribution of intermediate states for which $|(E_p - E_a)/k_B T| \ll 1$. This fact is noted in Ref. [5] in regard to the electric dipole shift and is established for the higher electric multipole shifts in Sec. II B. Thus $\delta E_a^{(EK)} \approx \delta E_a^{(EK)^\nu}$ for Rydberg states.

Evaluating the shifts $\delta E_a^{(EK)^\nu}$ is particularly simple as the summation over intermediate states can be done analytically. Indeed, as shown in Appendix A,

$$\begin{aligned} & \sum_{n_p l_p} (2l_p + 1) \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 (E_p - E_a) |\langle n_a l_a | r^K | n_p l_p \rangle|^2 \\ & = \frac{1}{2} K(2K+1) \langle a | r^{2K-2} | a \rangle \end{aligned} \quad (16)$$

for hydrogenic species. Thus

$$\begin{aligned} \delta E_a^{(EK)^\nu} = & \frac{1}{\pi} \frac{(K+1)(2K+1)!}{2K(2K+1)!!(2K-1)!!} \frac{(k_B T)^{2K}}{c^{2K+1}} \\ & \times \langle a | r^{2K-2} | a \rangle \end{aligned} \quad (17)$$

for hydrogen and one-electron ions. In particular,

$$\delta E_a^{(E1)^\nu} = \frac{\pi}{3} \frac{(k_B T)^2}{c^3} \quad (18)$$

for the electric dipole shift and

$$\delta E_a^{(E2)^\nu} = \frac{\pi^3 (k_B T)^4}{45 c^5} \langle a | r^2 | a \rangle \quad (19)$$

for the electric quadrupole shift. The numerical results presented in Sec. II B 4 indicate that Eq. (17) also holds for Rydberg states of other systems, at least approximately. Equation (18) applies generally [5].

It can be noted, by comparing Eq. (19) to Eq. (3), that $\delta E_a^{(E2)^\nu} = \delta E_a^{(E2)}$. However, it is shown in Sec. III B that $\delta E_a^{(E2)^\nu}$ is largely canceled by a term proportional to $(k_B T)^4 \langle a | r^2 | a \rangle / c^5$ contributed by retardation.

The magnetic multipole shifts $\delta E_a^{(MK)}$ are smaller by a factor $1/c^2$ compared to their electric multipole counterparts. They are considered in Sec. III C.

B. Numerical illustration

1. Methods

In the case of hydrogen, we calculate the electric dipole shift $\delta E_a^{(E1)}$ and electric quadrupole shift $\delta E_a^{(E2)}$ without retardation using the method outlined in Appendix D of Ref. [15]. That is, we construct the matrix $\mathbf{H}$ representing the nonrelativistic Hamiltonian in a basis of Sturmian functions and spherical harmonics and solve the corresponding generalized eigenvalues problem, $\mathbf{H}\mathbf{C}_k = w_k \mathbf{S}\mathbf{C}_k$, where $\mathbf{S}$ is the overlap matrix of the basis. The eigenvalues w_k effectively form a discrete representation of the whole spectrum of the atom, including its continuum part. We use 300 to 600 radial Sturmians for each value of l , which ensures an excellent agreement of all the 70 lowest values w_k with the corresponding eigenenergies of the exact Hamiltonian, $-1/2n_k^2$ with $n_k = l+1, l+2, \dots$. Doing so makes it possible to replace the summation over the intermediate states $|p\rangle$, which involves an integration over continuum states, by a simpler summation over the generalized eigenvectors of the matrix $\mathbf{H}$. The basis used in the calculation is large enough to ensure an excellent agreement between the resulting values of the matrix elements $\langle a | r | p \rangle$ and $\langle a | r^2 | p \rangle$ and their exact values [16] for all bound states of interest, an excellent agreement of the static dipole and quadrupole polarizabilities of these states with their analytical values [17], and an excellent agreement between the values of $\delta E^{(E1)^\nu}$ and $\delta E^{(E2)^\nu}$ calculated as per Eq. (15) and those calculated as per Eqs. (18) and (19). The method will be described in greater detail elsewhere [18].

This approach does not easily generalize to other atoms. We used the ARC program [19,20] to compute the state energies and quadrupole matrix elements required by the calculation of the BBR quadrupole shift in cesium reported in Sec. II B 4.

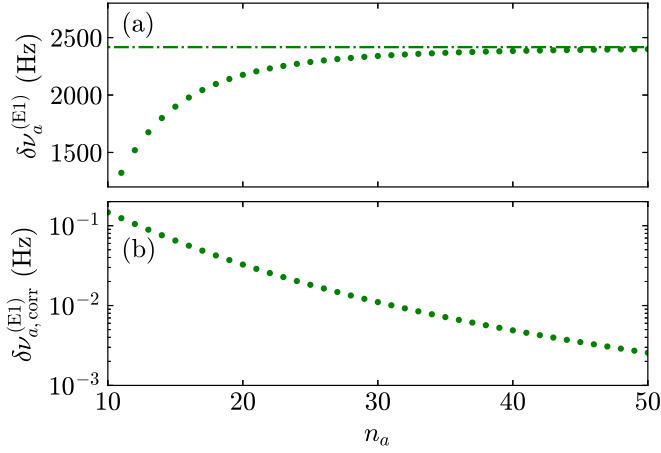


FIG. 1. (a) The electric dipole frequency shifts $\delta\nu_a^{(E1)}$ (markers) and $\delta\nu_a^{(E1) \prime}$ (dash-dotted line) of s states of hydrogen at 300 K vs the principal quantum number of the state. (b) The corresponding relativistic correction to the electric dipole shift as defined by Eq. (23).

Computing the shifts $\delta E_a^{(E1)}$ and $\delta E_a^{(E2)}$ also involves the calculation of the F_K function for $K = 1$ and 2. As in Ref. [15], we do this by contour integration in the complex plane.

For convenience, we state the resulting energy shifts in terms of the corresponding frequency shifts, and similarly for the energy shifts considered later in this paper:

$$\delta\nu_a^{(\cdot)} \equiv \delta E_a^{(\cdot)} / h, \quad \delta\nu_a^{(\cdot) \prime} \equiv \delta E_a^{(\cdot) \prime} / h, \quad (20)$$

where h is the Planck constant.

2. Electric dipole shift in hydrogen

For completeness, the variation of the electric dipole energy shifts $\delta E_a^{(E1)}$ with the principal quantum number of the state is illustrated by Fig. 1(a) for the case of s states of hydrogen at room temperature. [Figure 1(b) is discussed in Sec. II C.] As noted above and in Ref. [5], $\delta E_a^{(E1)}$ is well approximated by the n_a -independent shift of Eq. (18) for sufficiently high Rydberg states.

3. Electric quadrupole shift in hydrogen

How the BBR frequency shifts $\delta\nu_a^{(E2)}$ and $\delta\nu_a^{(E2) \prime}$ vary with principal quantum number in the case of hydrogen is shown in Figs. 2(a) and 2(b) ($T = 300$ K, as in Fig. 1). Only results for the s series are presented in Fig. 2, for clarity. The results for the p and d series are almost identical [18].

While very small for the low lying states, $\delta\nu_a^{(E2)}$ increases rapidly with n_a , roughly like n_a^4 , to reach values of the order of 1 Hz for $n_a \approx 50$ at the temperature considered [21]. Moreover, $\delta\nu_a^{(E2)}$ and $\delta\nu_a^{(E2) \prime}$ are almost equal for large values of n_a : these two shifts differ by less than 1% for $n_a \geq 20$ and the difference decreases as n_a increases. The rapid convergence of $\delta\nu_a^{(E2)}$ to $\delta\nu_a^{(E2) \prime}$ for high Rydberg states can be noted from Fig. 2(b). This figure also shows that $\delta\nu_a^{(E2)}$ converges to $\delta\nu_a^{(E2) \prime}$ faster than $\delta\nu_a^{(E1)}$ converges to $\delta\nu_a^{(E1) \prime}$.

The similarity between the values of $\delta\nu_a^{(E2)}$ and of $\delta\nu_a^{(E2) \prime}$ indicates that replacing $F_2(y)$ by its small- $|y|$ limit is a good approximation for the intermediate states contributing most to $\delta\nu_a^{(E2)}$, at least at 300 K. That this is indeed the case for high

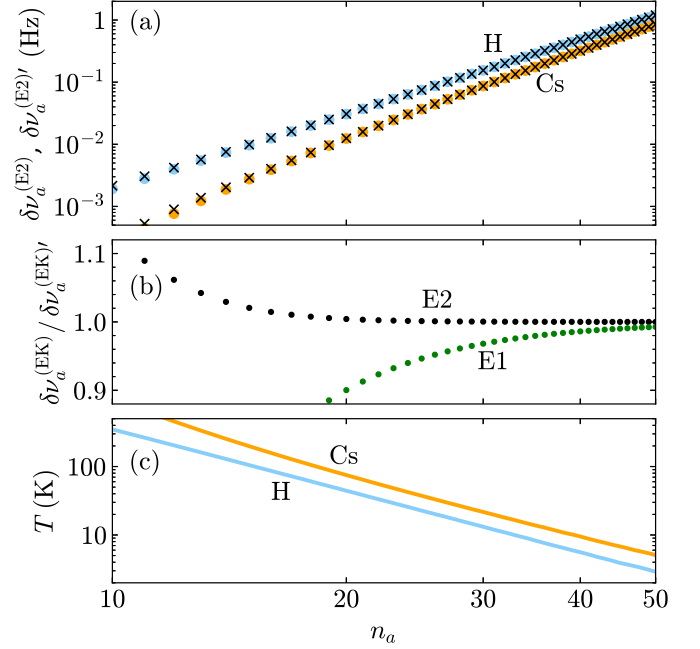


FIG. 2. (a) The electric quadrupole BBR shifts $\delta\nu_a^{(E2)}$ (crosses) and $\delta\nu_a^{(E2) \prime}$ (filled circles) of s states of hydrogen and cesium at 300 K vs the principal quantum number of the state. (b) The ratios $\delta\nu_a^{(E2)} / \delta\nu_a^{(E2) \prime}$ (black markers) and $\delta\nu_a^{(E1)} / \delta\nu_a^{(E1) \prime}$ (green markers) for the s states of hydrogen at 300 K. (c) The temperature below which $\delta\nu_a^{(E2) \prime}$ differs from $\delta\nu_a^{(E2)}$ by more than 10%.

Rydberg states is shown by the five-figure agreement between the values of $\delta\nu_a^{(E2)}$ and $\delta\nu_a^{(E2) \prime}$ given in the penultimate row of Table I. These two results were obtained by summing over all intermediate states, including those representing the discretized continuum, and are converged with respect to this summation to the number of digits given in the table. The converged value of $\delta\nu_a^{(E2) \prime}$ is itself in full agreement with the result predicted by Eq. (19).

TABLE I. Electric quadrupole BBR shift of the $50s$ state of hydrogen at a temperature of 300 K as calculated in various approximations. Retardation is neglected. $\delta\nu_a^{(E2)}$: results obtained when the $F_2(y)$ function is calculated according to its definition, Eq. (8). $\delta\nu_a^{(E2) \prime}$: results obtained when the $F_2(y)$ function is approximated by its small- $|y|$ limit, Eq. (13). The first five rows give the results obtained when the summation over the principal quantum number of the intermediate state is restricted to the range indicated. The penultimate row are the results obtained by summing over a complete set of intermediate states.

Range	$\delta\nu_a^{(E2)}$ (Hz)	$\delta\nu_a^{(E2) \prime}$ (Hz)
$48 \leq n_p \leq 52$	1.13113	1.13112
$46 \leq n_p \leq 54$	1.17300	1.17299
$44 \leq n_p \leq 56$	1.18321	1.18320
$42 \leq n_p \leq 58$	1.18732	1.18731
$40 \leq n_p \leq 60$	1.18941	1.18939
Limit	1.19428	1.19425
Eq. (19)		1.19425

TABLE II. The same as Table I but here for the electric quadrupole BBR shift of the ($n = 50, l = 49$) circular state.

Range	$\delta\nu_a^{(E2)}$ (Hz)	$\delta\nu_a^{(E2)^\vee}$ (Hz)
$48 \leq n_p \leq 52$	0.26698	0.26699
$48 \leq n_p \leq 54$	0.48887	0.48884
$48 \leq n_p \leq 56$	0.49197	0.49194
$48 \leq n_p \leq 58$	0.49210	0.49208
$48 \leq n_p \leq 60$	0.49211	0.49209
Eq. (19)		0.49209

How these converged values build up when summing over the intermediate states is illustrated by the first five rows of the table, which give the shifts as calculated when this summation is restricted to the range of principal quantum numbers indicated. The energy shift of these large- n_a states is largely contributed by intermediate states with $n_p \approx n_a$. The argument of the $F_2(y)$ function is close to zero for such intermediate states. E.g., at 300 K, $|(E_p - E_a)/k_B T|$ is at most 0.12 for $40 \leq n_p \leq 60$ when $n_a = 50$. The agreement between $\delta\nu_a^{(E2)}$ and $\delta\nu_a^{(E2)^\vee}$ shows that the intermediate states with a higher energy difference do not contribute enough for invalidating the replacement of $F_2(y)$ by its small- $|y|$ form. The sum over intermediate state converges rapidly for lower states, too: when $n_a \leq 10$, and for $T = 300$ K, the value of $\delta\nu_a^{(E2)}$ calculated with n_p limited to the range $[n_a - 10, n_a + 10]$ never differs from the converged value by more than 0.5%. Convergence is also found for states of high orbital angular momentum quantum numbers such as circular Rydberg states (Table II).

Since the argument of the F_2 function is inversely proportional to $k_B T$, the approximation made by replacing $F_2(y)$ by its small- y form deteriorates when T decreases. As can be seen from Fig. 2(c), it remains nonetheless good down to temperatures close to 3 K for $n_a \gtrsim 50$.

4. Electric quadrupole shift in cesium

The small importance of the intermediate states outside the $[n_a - 10, n_a + 10]$ range noted above for the quadrupole shift of hydrogen suggests that these states may also be neglected, in good approximation, when calculating the quadrupole BBR shift of the Rydberg states of alkali metals. Doing so for cesium yields the other set of results shown in Fig. 2(a), for which the $\delta\nu_a^{(E2)^\vee}$ shifts are now represented by orange markers rather than by blue markers.

The results are qualitatively the same as for hydrogen, although the conditions of applicability of the proof of Eq. (16) given in Appendix A are not strictly met here (we take the fine-structure splitting into account and ARC uses different model potentials for different series when calculating the radial wave functions, while the proof assumes no fine-structure splitting and the same potential for all relevant series).

5. Higher multipole shifts

We have also evaluated the higher-order multipole contributions to the BBR shift of hydrogen up to $K = 8$, here by summing the contributions of bound intermediate states energetically close to the state of interest rather than by

TABLE III. $K = 8$ electric multipole BBR shift of the 50s state of hydrogen at a temperature of 300 K as calculated in various approximations. Retardation is neglected. $\delta\nu_a^{(E8)}$: results obtained when the $F_8(y)$ function is calculated according to its definition, Eq. (8). $\delta\nu_a^{(E8)^\vee}$: results obtained when the $F_8(y)$ function is approximated by its small- $|y|$ limit, Eq. (13). As in Table I, the first five rows give the results obtained when the summation over the principal quantum number of the intermediate state is restricted to the range indicated.

Range	$\delta\nu_a^{(E8)}$ (10^{-18} Hz)	$\delta\nu_a^{(E8)^\vee}$ (10^{-18} Hz)
$48 \leq n_p \leq 52$	2.25360	2.25360
$46 \leq n_p \leq 54$	2.25424	2.25424
$44 \leq n_p \leq 56$	2.25433	2.25432
$42 \leq n_p \leq 58$	2.25433	2.25433
$40 \leq n_p \leq 60$	2.25433	2.25433
Eq. (17)		2.25433

summing the contributions of a large number of Sturmian basis functions [16]. We found that the higher multipole BBR shifts of Rydberg states are also dominated by the contributions of neighboring intermediate states for which $|E_p - E_a|/k_B T \ll 1$. For instance, including only intermediate states with $n_a - 10 \leq n_p \leq n_a + 10$ in the sum is sufficient for obtaining values of the shifts $\delta E^{(EK)^\vee}$ verifying Eq. (17) to six significant digits for $n_a \approx 50$. In fact, the higher K is, the more dominant the neighboring states are, e.g., compare the results given in Table I for the quadrupole shift with those given in Table III for the $K = 8$ shift. As a result, the multipole shifts $\delta E^{(EK)}$ are increasingly well approximated by $\delta E^{(EK)^\vee}$, thus by the right-hand side of Eq. (17): for all practical purposes,

$$\delta E_a^{(EK)} = \frac{1}{\pi} \frac{2^{2K-1} (K-1)! (K+1)!}{(2K)!} \zeta(2K) \times \frac{(k_B T)^{2K}}{c^{2K+1}} \langle a | r^{2K-2} | a \rangle, \quad K \geq 2, n_a \gg 10. \quad (21)$$

This approximation improves not only when K increases for a fixed temperature but also when T increases for a fixed K (these high multipole shifts increase rapidly with T and are numerically significant for $T \approx T_a$).

C. Relativistic corrections

We estimate the importance of the relativistic corrections to $\delta E_a^{(E1)}$ and $\delta E_a^{(E2)}$ in hydrogen by repeating the above calculations with the nonrelativistic Hamiltonian, H , replaced by the Breit-Pauli Hamiltonian, H_{BP} :

$$H_{BP} = H - \frac{\mathbf{p}^4}{8c^2} + \frac{1}{2c^2} \frac{\mathbf{L} \cdot \mathbf{S}}{r^3} + \frac{\pi}{2c^2} \delta(\mathbf{r}), \quad (22)$$

where $\mathbf{p}$, $\mathbf{L}$, and $\mathbf{S}$ are the momentum operator, orbital angular momentum operator, and spin operator of the electron. The Breit-Pauli Hamiltonian is consistent with the Dirac Hamiltonian to order $1/c^2$. Diagonalizing it on the Sturmian basis and using the resulting wave functions and energies in Eq. (7) yields electric dipole shifts $\delta E_{a,BP}^{(E1)}$ and electric quadrupole shifts $\delta E_{a,BP}^{(E2)}$. These shifts differ from their nonrelativistic counterparts by terms of order $1/c^2$ as well as by terms of higher order in $1/c^2$. The latter are not consistent with a

formulation based on the Breit-Pauli Hamiltonian. However, they are negligible for the states considered. We can therefore quantify the importance of the relativistic corrections to the electric dipole shift by the difference $\delta E_{a,\text{BP}}^{(\text{E1})} - \delta E_a^{(\text{E1})}$, or equivalently by the corresponding frequency shift $\delta \nu_{a,\text{corr}}^{(\text{E1})}$:

$$\delta \nu_{a,\text{corr}}^{(\text{E1})} = [\delta E_{a,\text{BP}}^{(\text{E1})} - \delta E_a^{(\text{E1})}] / h, \quad (23)$$

where $\delta E_a^{(\text{E1})}$ is the shift calculated nonrelativistically. The small importance of the relativistic corrections for the Rydberg states and temperatures considered in the present work is borne out by Fig. 1(b). E.g., at 300 K, $\delta \nu_{a,\text{corr}}^{(\text{E1})} \approx 3$ mHz for the 50s state. By contrast, $\delta \nu_a^{(\text{E2})}$ and the leading retardation correction to $\delta \nu_a^{(\text{E2})}$ are both of the order of 1 Hz for that state at this temperature. We will thus neglect these relativistic corrections in the following. However, we note that these corrections may exceed the quadrupole and diamagnetic BBR shifts for much lower excited states and/or for cryogenic temperatures.

The relativistic corrections to the electric quadrupole shift $\delta E_a^{(\text{E2})}$ are also negligible for our purposes, e.g., $\delta E_{a,\text{BP}}^{(\text{E2})}$ differs from $\delta E_a^{(\text{E2})}$ by not more than 0.003% for any s state with $n_a \geq 10$ at room temperature.

III. BBR SHIFT WITH RETARDATION

A. Nonrelativistic theory

We start by considering the ac Stark shift of a state $|a\rangle$ induced by an electromagnetic field with wave vector $\mathbf{k}$ and polarization vector $\hat{\epsilon}$ ($|\mathbf{k}| = k = \omega/c$, $\mathbf{k} \cdot \hat{\epsilon} = 0$, and $\hat{\epsilon} \cdot \hat{\epsilon}^* = 1$). Following Ref. [10], we define its electric-field and magnetic-field components by the equations

$$\mathbf{E}_{\mathbf{k}}(\mathbf{r}, t) = \frac{\mathcal{E}}{2} \{ \hat{\epsilon} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] + \text{c.c.} \}, \quad (24a)$$

$$\mathbf{B}_{\mathbf{k}}(\mathbf{r}, t) = \frac{\mathcal{E}}{2c} \{ \hat{\beta} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] + \text{c.c.} \}, \quad (24b)$$

with $\hat{\beta} = \mathbf{k} \times \hat{\epsilon} / k$. The Hamiltonian of a one-electron system in the presence of this field takes up the following form in the Power-Zienau-Woolley gauge [22–25]:

$$H = \frac{1}{2} \left[-i\nabla - \int_0^1 \mathbf{r} \times \mathbf{B}_{\mathbf{k}}(\lambda \mathbf{r}, t) \lambda d\lambda \right]^2 + V(r) + \int_0^1 \mathbf{r} \cdot \mathbf{E}_{\mathbf{k}}(\lambda \mathbf{r}, t) d\lambda. \quad (25)$$

To second order in $\mathcal{E}$, the electric and magnetic fields $\mathbf{E}_{\mathbf{k}}(\mathbf{r}, t)$ and $\mathbf{B}_{\mathbf{k}}(\mathbf{r}, t)$ shift the energy of state $|a\rangle$ by $\delta E_a(\mathcal{E}, \mathbf{k}, \hat{\epsilon})$. This Stark shift can be written as the sum of an electric multipole shift $\delta E_a(\mathcal{E}, \mathbf{k}, \hat{\epsilon})$, a paramagnetic shift $\delta E_a^{(\text{P})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon})$, and a diamagnetic shift $\delta E_a^{(\text{D})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon})$:

$$\delta E_a(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) = \delta E_a^{(\text{E})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) + \delta E_a^{(\text{P})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) + \delta E_a^{(\text{D})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) \quad (26)$$

with [10]

$$\delta E_a^{(\text{E})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) = (\mathcal{E}/2)^2 \sum_p \left(\frac{\langle a | v_E | p \rangle \langle p | v_E^\dagger | a \rangle}{\omega_{ap} - \omega} + \frac{\langle a | v_E^\dagger | p \rangle \langle p | v_E | a \rangle}{\omega_{ap} + \omega} \right), \quad (27a)$$

$$\delta E_a^{(\text{P})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon})$$

$$= (\mathcal{E}/2c)^2 \sum_p \left(\frac{\langle a | v_M | p \rangle \langle p | v_M^\dagger | a \rangle}{\omega_{ap} - \omega} + \frac{\langle a | v_M^\dagger | p \rangle \langle p | v_M | a \rangle}{\omega_{ap} + \omega} \right), \quad (27b)$$

and

$$\delta E_a^{(\text{D})}(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) = (\mathcal{E}/2c)^2 \langle a | v_D | a \rangle. \quad (27c)$$

In these equations,

$$v_E \equiv \int_0^1 \mathbf{r} \cdot \hat{\epsilon} \exp(i\lambda \mathbf{k} \cdot \mathbf{r}) d\lambda, \quad (28a)$$

$$v_M \equiv \frac{i}{2} \int_0^1 \{ \nabla \cdot [\mathbf{r} \times \hat{\beta} \exp(i\lambda \mathbf{k} \cdot \mathbf{r})] + [\mathbf{r} \times \hat{\beta} \exp(i\lambda \mathbf{k} \cdot \mathbf{r})] \cdot \nabla \} \lambda d\lambda, \quad (28b)$$

$$v_D \equiv (\mathbf{r} \times \hat{\beta}) \cdot (\mathbf{r} \times \hat{\beta}^*) \times \int_0^1 \int_0^1 \exp[i(\lambda - \lambda') \mathbf{k} \cdot \mathbf{r}] \lambda \lambda' d\lambda d\lambda', \quad (28c)$$

and

$$\omega_{ap} = E_a - E_p. \quad (29)$$

The interaction v_M can also be written in the following form:

$$v_M \equiv \frac{1}{2} \int_0^1 [\mathbf{L} \cdot \hat{\beta} \exp(i\lambda k z) + \exp(i\lambda k z) \hat{\beta} \cdot \mathbf{L}] \lambda d\lambda, \quad (30)$$

where $\mathbf{L}$ is the orbital angular momentum operator.

Let us assume that state $|a\rangle$ has a well-defined magnetic quantum number m_a^L in a system of axes, the L system, which is fixed with respect to the laboratory. As shown by Eqs. (26)–(29),

$$\delta E_a(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) = \left(\frac{\mathcal{E}}{2} \right)^2 \langle n_a l_a m_a^L | \mathcal{V}(\mathbf{k}, \hat{\epsilon}) | n_a l_a m_a^L \rangle, \quad (31)$$

where $\mathcal{V}(\mathbf{k}, \hat{\epsilon})$ is a certain operator. Let us also consider another system of axes, the S system, whose z axis is along the wave vector $\mathbf{k}$ and whose xy plane is subtended by the vectors $\hat{\epsilon}$ and $\hat{\beta}$. The L system can be brought to the S system by a rotation with Euler angles α , β , and γ . This rotation would transform $|n_a l_a m_a^L\rangle$ into a linear combination of eigenvectors $|n_a l_a m_a\rangle$ of the z component of $\mathbf{L}$ in the S system. In terms of Wigner rotation matrices,

$$|n_a l_a m_a^L\rangle = \sum_{m_a} \mathcal{D}_{m_a^L m_a}^{(l_a)}(\alpha, \beta, \gamma) |n_a l_a m_a\rangle. \quad (32)$$

Therefore,

$$\delta E_a(\mathcal{E}, \mathbf{k}, \hat{\epsilon}) = \left(\frac{\mathcal{E}}{2} \right)^2 \sum_{m_a' m_a} \mathcal{D}_{m_a' m_a}^{(l_a)*}(\alpha, \beta, \gamma) \mathcal{D}_{m_a' m_a}^{(l_a)}(\alpha, \beta, \gamma) \times \langle n_a l_a m_a' | \mathcal{V}(\mathbf{k}, \hat{\epsilon}) | n_a l_a m_a \rangle. \quad (33)$$

Assuming that the BBR field is both unpolarized and isotropic, the BBR shift of state $|a\rangle$, δE_a , can then be obtained by averaging $\delta E_a(\mathcal{E}, \mathbf{k}, \hat{\epsilon})$ over the three Euler angles and over the frequency spectrum of the BBR field. To this end, we

equate the power density $(\mathcal{E}/2)^2/2\pi$ to $u(\omega, T) d\omega$ [10], with

$$u(\omega, T) = \frac{1}{\pi^2 c^3} \frac{\omega^3}{\exp(\omega/k_B T) - 1}, \quad (34)$$

and write

$$\begin{aligned} \delta E_a &= \frac{2}{\pi c^3} \int_0^\infty \frac{\omega^3 d\omega}{\exp(\omega/k_B T) - 1} \frac{1}{8\pi^2} \int_0^{2\pi} d\alpha \int_0^\pi d\beta \sin \beta \\ &\times \int_0^{2\pi} d\gamma \delta E_a(\mathcal{E}, \mathbf{k}, \hat{\mathbf{e}}). \end{aligned} \quad (35)$$

Integrating over α , β , and γ collapses the sum over m'_a into a single term due to the orthogonality of the rotation matrices. The result is

$$\begin{aligned} \delta E_a &= \frac{2}{\pi c^3} \int_0^\infty \frac{\omega^3 d\omega}{\exp(\omega/k_B T) - 1} \frac{1}{2l_a + 1} \\ &\times \sum_{m_a} \langle n_a l_a m_a | \mathcal{V}(\mathbf{k}, \hat{\mathbf{e}}) | n_a l_a m_a \rangle, \end{aligned} \quad (36)$$

where $\hat{\mathbf{e}}$ is an arbitrary unit vector in the xy plane and it is understood that the vector $\mathbf{k}$ is in the positive z direction. As expected since the BBR field is isotropic, δE_a does not depend on m_a^L .

As above, the BBR shift δE_a is the sum of an electric multipole shift $\delta E_a^{(E)}$, a paramagnetic shift $\delta E_a^{(P)}$, and a diamagnetic shift $\delta E_a^{(D)}$:

$$\delta E_a = \delta E_a^{(E)} + \delta E_a^{(P)} + \delta E_a^{(D)}. \quad (37)$$

We consider each of these three terms in the next sections and in Appendixes B–D. The details of the calculation depend on the choice of polarization vector $\hat{\mathbf{e}}$ but the final results do not.

B. Electric multipole shift

The calculation of $\delta E_a^{(E)}$ is outlined in Appendix B. In view of the results of Sec. II, it can be expected that for a Rydberg state $|a\rangle$, $\delta E_a^{(E)}$ is dominated by the contribution of intermediate states $|p\rangle$ close in energy to this state and such that $|E_p - E_a|/(k_B T) \ll 1$. Retaining only the term of leading order in $|E_p - E_a|/(k_B T)$ in the calculation amounts to approximating $\delta E_a^{(E)}$ by $\delta E_a^{(E) \prime}$, where $\delta E_a^{(E) \prime}$ is given by Eqs. (B15) and (B16). The right-hand side of this last equation can be recast as a simpler series of powers in $k_B T/c$, namely,

$$\delta E_a^{(E) \prime} = \sum_{n=1}^{\infty} c_n^{(E)} \frac{(k_B T)^{2n}}{c^{2n+1}} \langle n_a l_a | r^{2n-2} | n_a l_a \rangle. \quad (38)$$

The coefficients of this series do not depend on T , n_a , or l_a and have the following general form:

$$c_n^{(E)} = \frac{1}{\pi} (a_n^{(E)} / b_n^{(E)}) \zeta(2n), \quad (39)$$

where $a_n^{(E)}$ and $b_n^{(E)}$ are integers [26].

The BBR shift $\delta E_a^{(E) \prime}$ thus depends on the temperature in a remarkably simple way. The leading term in its expansion in powers of $(k_B T)/c$ is the asymptotic BBR shift $\delta E_a^{(E1) \prime}$ found in the dipole approximation [5,9] ($c_1^{(E)} = \pi/3$). The next term is the sum of the partial shifts $\delta E_{a,00}^{(E2) \prime}$, $\delta E_{a,10}^{(E1) \prime}$, and $\delta E_{a,01}^{(E1) \prime}$ of Eq. (B15), i.e., the electric quadrupole shift $\delta E_a^{(E2) \prime}$ of Eq. (19)

and the leading-order retardation corrections to the electric dipole shift. These three terms contribute, respectively, $\pi^3/45$, $-\pi^3/135$, and $-\pi^3/135$ to the coefficient $c_2^{(E)}$, which gives $c_2^{(E)} = \pi^3/135$. The latter two terms thus largely cancel the electric quadrupole shift $\delta E_a^{(E2)}$.

Calculating $\delta E_a^{(E) \prime}$ by direct summation of the right-hand side of Eq. (38) may be problematic because the matrix elements $\langle n_a l_a | r^{2n-2} | n_a l_a \rangle$ increase exponentially when $n_a \rightarrow \infty$ while the factors multiplying these matrix elements decrease only slowly. These two expansions are divergent and asymptotic. The difficulty can be traced to Eq. (B11), which formulates $\delta E_a^{(E) \prime}$ as a sum of integrals of $u(\omega, T)$ multiplied by a power of ω rather than as the integral of $u(\omega, T)$ multiplied by a function of ω . It can be avoided by using the fact that

$$\int_0^\infty \frac{\omega^{2n-1} d\omega}{\exp(\omega/k_B T) - 1} = (2n-1)! \zeta(2n) (k_B T)^{2n} \quad (40)$$

and writing Eq. (38) in the following form, which does not involve an exponentially divergent series:

$$\begin{aligned} \delta E_a^{(E) \prime} &= \int_0^\infty \frac{d\omega}{\exp(\omega/k_B T) - 1} \\ &\times \frac{1}{\pi} \sum_{n=1}^{\infty} \frac{a_n^{(E)} / b_n^{(E)}}{(2n-1)!} \frac{\omega^{2n-1}}{c^{2n+1}} \langle n_a l_a | r^{2n-2} | n_a l_a \rangle. \end{aligned} \quad (41)$$

C. Paramagnetic shift

The paramagnetic shift without retardation is normally negligible for Rydberg states [10]. The paramagnetic shift with retardation, $\delta E_a^{(P)}$, can be calculated in the same way as the electric shift $\delta E_a^{(E)}$. Like the latter, we can approximate $\delta E_a^{(P)}$ by a shift $\delta E_a^{(P) \prime}$, assuming that the states and temperatures considered are such that $\delta E_a^{(P)}$ is dominated by the contribution of intermediate states for which $|E_p - E_a| \ll k_B T$. Proceeding as above yields $\delta E_a^{(P) \prime}$ as a power series of the following form:

$$\delta E_a^{(P) \prime} = \sum_{n=2}^{\infty} C_n^{(P)}(n_a, l_a) \frac{(k_B T)^{2n}}{c^{2n+3}}, \quad (42)$$

where the coefficients $C_n^{(P)}(n_a, l_a)$ vary from state to state but do not depend on T . Each term in this series is a factor $1/c^2$ smaller than the term of the same order in $k_B T$ in the expansion of $\delta E_a^{(E) \prime}$. The paramagnetic shift can therefore be expected to be very small compared to the electric multipole shift even when retardation is taken into account. Moreover, as each of the terms in the expansion of $\delta E_a^{(P) \prime}$ is of the same order in $1/c$ as the relativistic corrections neglected in the present calculations, these corrections would also need to be taken into account in a consistent treatment of the BBR shift to that order in $1/c$.

The coefficients $C_n^{(P)}(n_a, l_a)$ are worked out in Appendix C for the specific case of s states ($l_a = 0$). The calculation results in a power series similar to that of Eq. (38):

$$\delta E_a^{(P)} = \sum_{n=2}^{\infty} c_n^{(P)} \frac{(k_B T)^{2n}}{c^{2n+3}} \langle n_a l_a | r^{2n-2} | n_a l_a \rangle \quad (43)$$

with

$$c_n^{(P)} = \frac{1}{\pi} (a_n^{(P)} / b_n^{(P)}) \zeta(2n), \quad (44)$$

where $a_n^{(P)}$ and $b_n^{(P)}$ are integers [26]. However, the calculation does not straightforwardly generalize to non- s states.

D. Diamagnetic shift

The calculation of $\delta E_a^{(D)}$ is outlined in Appendix D. This shift takes on a form similar as that found for the electric multipole shift $\delta E_a^{(E)}$, i.e.,

$$\delta E_a^{(D)} = \sum_{n=2}^{\infty} c_n^{(D)} \frac{(k_B T)^{2n}}{c^{2n+1}} \langle n_a l_a | r^{2n-2} | n_a l_a \rangle. \quad (45)$$

The coefficients $c_n^{(D)}$ are easily calculated. Like the coefficients $c_n^{(E)}$ of the expansion of the shift $\delta E_a^{(E)}$, they do not depend on T , n_a , or l_a . They also have the same general form,

$$c_n^{(D)} = \frac{1}{\pi} (a_n^{(D)} / b_n^{(D)}) \zeta(2n), \quad (46)$$

where $a_n^{(D)}$ and $b_n^{(D)}$ are integers [26]. The first term in this series is of order $(k_B T)^4$ and has $c_2^{(D)} = \pi^3/45$, in complete agreement with Eq. (3). The higher-order terms originate from retardation.

The right-hand side of Eq. (45) is an asymptotic series, like the right-hand side of Eq. (38). Calculations of the diamagnetic shift requiring a summation of this series to a large number of terms may thus be best based on the following equation, which avoids the exponential divergence affecting Eq. (45):

$$\delta E_a^{(D)} = \int_0^{\infty} \frac{d\omega}{\exp(\omega/k_B T) - 1} \times \frac{1}{\pi} \sum_{n=1}^{\infty} \frac{a_n^{(D)} / b_n^{(D)}}{(2n-1)!} \frac{\omega^{2n-1}}{c^{2n+1}} \langle n_a l_a | r^{2n-2} | n_a l_a \rangle. \quad (47)$$

This shift is always positive, as can be seen from the structure of Eq. (D7).

E. Total BBR shift

It follows from the above that the BBR shift of a Rydberg state $|a\rangle$ is closely approximated by the sum of the electric multipole shift $\delta E_a^{(E)}$ and the diamagnetic shift $\delta E_a^{(D)}$:

$$\delta E_a \approx \delta E_a^{(E)} + \delta E_a^{(D)}. \quad (48)$$

Thus, from Eqs. (18), (41), and (47),

$$\delta E_a \approx \delta E_a^d + \delta E_a^{\text{nd}} \quad (49)$$

where δE_a^d is the asymptotic electric dipole shift [5,9],

$$\delta E_a^d = \delta E_a^{(E1)} = \frac{\pi}{3} \frac{(k_B T)^2}{c^3}, \quad (50)$$

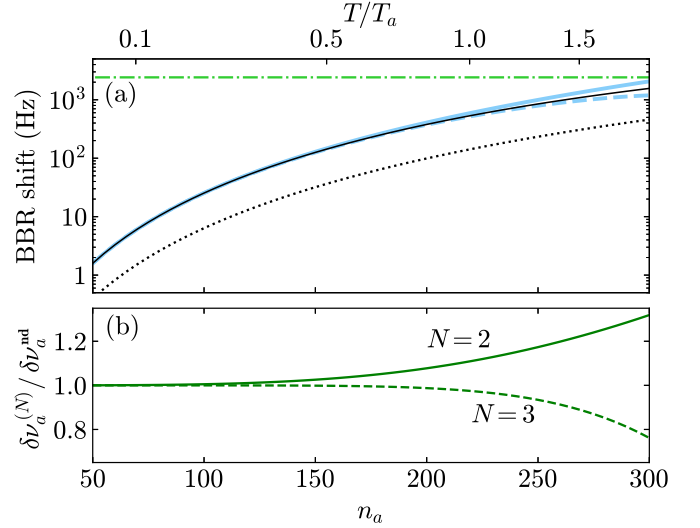


FIG. 3. (a) The BBR shift of s states of hydrogen at 300 K vs the principal quantum number of the state. Solid black curve: the total nondipole shift, δE_a^{nd} . Dotted black curve: the contribution of the electric multipole shift to the total nondipole shift. Solid blue curve: the nondipole shifts $\delta E_a^{(2)}$. Dashed blue curve: the nondipole shift $\delta E_a^{(3)}$. Dash-dotted line: the dipole shift, δE_a^d . (b) The ratio of either the $\delta E_a^{(2)}$ shift (upper curve) or the $\delta E_a^{(3)}$ shift (lower curve) to the total nondipole shift for the same states and temperature as in (a).

and δE_a^{nd} is a nondipole contribution to the BBR shift: as an integral,

$$\delta E_a^{\text{nd}} = \int_0^{\infty} \frac{\omega d\omega}{\exp(\omega/k_B T) - 1} \times \frac{1}{\pi} \sum_{n=2}^{\infty} \left(\frac{a_n^{(E)}}{b_n^{(E)}} + \frac{a_n^{(D)}}{b_n^{(D)}} \right) \frac{\omega^{2n-2}}{c^{2n+1}} \frac{\langle n_a l_a | r^{2n-2} | n_a l_a \rangle}{(2n-1)!}, \quad (51)$$

or as an asymptotic series,

$$\delta E_a^{\text{nd}} = \sum_{n=2}^{\infty} (c_n^{(E)} + c_n^{(D)}) \frac{(k_B T)^{2n}}{c^{2n+1}} \langle n_a l_a | r^{2n-2} | n_a l_a \rangle. \quad (52)$$

Taking into account only the first term in this last series gives an approximation of order $(k_B T)^4$ to the nondipole shift, namely,

$$\delta E_a^{(2)} = \frac{8\pi^3}{135} \frac{(k_B T)^4}{c^5} \langle a | r^2 | a \rangle. \quad (53)$$

Keeping the first two terms gives an approximation of order $(k_B T)^6$:

$$\delta E_a^{(3)} = \frac{8\pi^3}{135} \frac{(k_B T)^4}{c^5} \langle a | r^2 | a \rangle - \frac{44\pi^5}{42525} \frac{(k_B T)^6}{c^7} \langle a | r^4 | a \rangle. \quad (54)$$

Numerical values of the nondipole BBR shift δE_a^{nd} of s states of hydrogen are presented in Figs. 3–5. We used

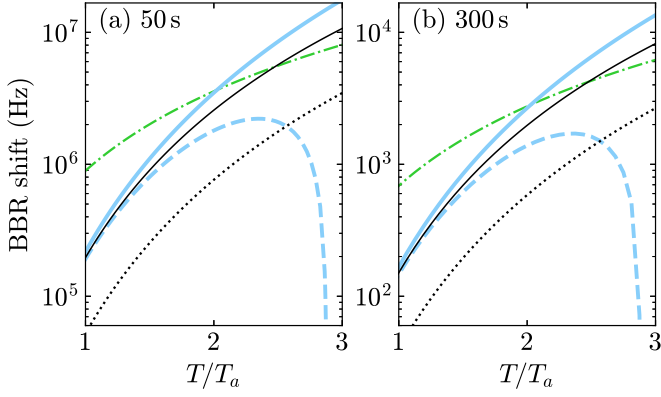


FIG. 4. As in Fig. 3(a), but here for the variation of the BBR shift with temperature for either the 50s or 300s state. The temperature is normalized to the characteristic temperature for the onset of retardation effect, T_a ($T_a = 5770$ K for the 50s state and 160 K for the 300s state).

the recursion relation [27]

$$\begin{aligned} \langle n_a l_a | r^k | n_a l_a \rangle = & \frac{(2k+1)n_a^2}{k+1} \langle n_a l_a | r^{k-1} | n_a l_a \rangle \\ & - \frac{k n_a^2}{4(k+1)} [(2l_a+1)^2 - k^2] \langle n_a l_a | r^{k-2} | n_a l_a \rangle \end{aligned} \quad (55)$$

to calculate the required radial matrix elements, starting with $\langle n_a l_a | n_a l_a \rangle = 1$ and

$$\langle n_a l_a | r | n_a l_a \rangle = [3n_a^2 - l_a(l_a+1)]/2. \quad (56)$$

We used both Eqs. (51) and (52) to calculate δE_a^{nd} . In the case of Eq. (51), we used Padé approximants for summing up the series [28]. Obtaining all the results presented in the figures required including up to the first 44 terms of the series in the summation. Numerically integrating the result over ω presented no difficulty.

Figures 3 and 4 illustrate the growing importance of the higher-order terms in the expansion of the full nondipole shift for increasing temperatures and increasing principal quantum numbers. The temperature T_a appearing in these figures is the characteristic temperature for the onset of retardation defined

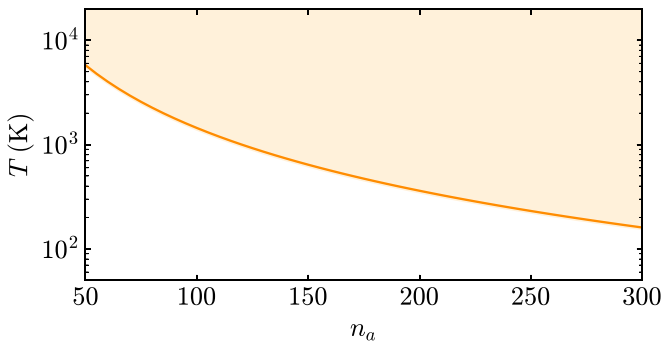


FIG. 5. Solid curve: the characteristic temperature for the onset of retardation effects, T_a . Shaded area: the temperature region in which the total nondipole shift δE_a^{nd} differs from $\delta E_a^{(2)}$ by more than 10%.

by Eq. (1). Figure 3 shows how the nondipole BBR shift at $T = 300$ K varies with n_a , whereas Fig. 4 shows how the nondipole BBR shift of the 50s and 300s states varies with T . As in Fig. 2, we report the energy shifts of interest in terms of the corresponding frequency shifts—thus in terms of the frequency shifts $\delta \nu_a^{\text{nd}}$, $\delta \nu_a^{(2)}$, $\delta \nu_a^{(3)}$, and $\delta \nu_a^{\text{d}}$ rather than in terms of the energy shifts δE_a^{nd} , $\delta E_a^{(2)}$, $\delta E_a^{(3)}$, and δE_a^{d} . The nondipole shifts $\delta \nu_a^{\text{nd}}$, $\delta \nu_a^{(2)}$, and $\delta \nu_a^{(3)}$ are represented, respectively, by the solid black curves, solid blue curves, and dashed blue curves. The dipole shift $\delta \nu_a^{\text{d}}$ is represented by the dash-dotted green curves and the contribution of the electric multipole shift to $\delta \nu_a^{\text{nd}}$ by the dotted black curves. We note that the electric multipole shift contributes only to between a quarter and a third of the full nondipole shift, at least at the temperatures considered. The latter is thus dominated by the diamagnetic shift.

As shown by these results, the ratio of the temperature to the state-dependent characteristic temperature T_a is a good indicator of the importance of the higher nondipole corrections: $\delta \nu_a^{\text{nd}} \approx \delta \nu_a^{(2)}$ when $T/T_a \ll 1$, whereas $\delta \nu_a^{\text{nd}}$ departs significantly from $\delta \nu_a^{(2)}$ when $T/T_a \gg 1$. The temperature T_a is practically identical to the temperature above which $\delta \nu_a^{\text{nd}}$ differs from $\delta \nu_a^{(2)}$ by more than 10% (Fig. 5).

Including the next-to-leading term in the calculation, as in Eq. (54), gives a value of the nondipole shift differing from the full nondipole shift by more than 10% only above $T/T_a \approx 1.5$, e.g., compare the dashed blue curves to the black solid curves in Figs. 3(a) and 4, and see Fig. 3(b). The difference increases rapidly with T , particularly above $2T_a$. The series (52) strongly diverges at these high temperatures. The full nondipole shift can still be calculated from Eq. (51), though. As shown by Fig. 4, it remains positive and continues to increase monotonically above $2T_a$, at least up to $T = 3T_a$. The nondipole shift becomes larger than the dipole shift $\delta \nu_a^{\text{d}}$ at $T \approx 2.5T_a$. The BBR shift is thus dominated by nondipole couplings at still higher temperatures.

IV. CONCLUSIONS

In summary, we have shown that the electric field of the thermal radiation contributes a shift identical in structure and of the same order in $k_B T/c$ as the diamagnetic BBR shift of Eq. (3). Albeit smaller in magnitude, this contribution may need to be taken into account in circumstances where the diamagnetic shift is relevant. More generally, we have studied how the familiar electric dipole formulation of the BBR shift can be extended to encompass retardation so as to make it possible to explore higher-temperature regimes. The calculations are largely based on the observation that the electric multipole shifts are dominated by the contribution of intermediate states close in energy to the state of interest. This makes it possible to replace the functions $F_K(y)$ and $F_{Kqq'}(y)$ of Eqs. (8) and (B13) by their small- $|y|$ forms. In turn, this makes it possible to reduce the electric multipole shifts with retardation to a remarkably simple form. The diamagnetic shift with retardation can be similarly simplified. The approximation improves when the temperature increases, which is also when corrections to the electric dipole BBR shift become relevant. Altogether, and as anticipated in Ref. [5], the BBR shift needs to be calculated beyond the electric dipole

approximation at temperatures close to or exceeding the characteristic temperature of Eq. (1). For atomic hydrogen, the total BBR shift is dominated by nondipole contributions at temperatures above $2.5 T_a$.

It would be of interest to extend these numerical calculations to other species, in particular to alkali metals. We have shown that the sum rules used in the present work are exact in the case of single active electron systems described by an l - and j -dependent model potential. The results for cesium presented in Sec. II B 4 indicate that these sum rules and the dominance of neighboring intermediate states also hold for the electric quadrupole shift of alkali metals. The above results for the full BBR shift of hydrogen are thus likely to extend to these more complex systems, at least qualitatively. However, a calculation of the higher-order BBR shifts would be necessary for reaching a definitive conclusion on this issue.

DATA AVAILABILITY

The data that support the findings of this article are openly available [26]; embargo periods may apply.

APPENDIX A: SUM RULES USED IN THIS WORK

The following sum rules underpin many of the calculations outlined in the body of the text and in Appendixes B and C:

$$\begin{aligned} \sum_{n_p} (E_p - E_a) \langle a | r^{k_1} | p \rangle \langle p | r^{k_2} | a \rangle \\ = \frac{1}{2} [k_1 k_2 + l_p(l_p + 1) - l_a(l_a + 1)] \langle a | r^{k_1 + k_2 - 2} | a \rangle \end{aligned} \quad (\text{A1})$$

and

$$\begin{aligned} \sum_{n_p l_p} (2l_p + 1) \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 (E_p - E_a) \langle a | r^{k_1} | p \rangle \langle p | r^{k_2} | a \rangle \\ = \frac{1}{2} [k_1 k_2 + K(K + 1)] \langle a | r^{k_1 + k_2 - 2} | a \rangle. \end{aligned} \quad (\text{A2})$$

More generally,

$$\begin{aligned} \sum_{n_p} (E_p - E_a) \langle a | f(r) | p \rangle \langle p | g(r) | a \rangle \\ = \frac{1}{2} \left\langle a \left| \frac{df}{dr} \frac{dg}{dr} + [l_p(l_p + 1) - l_a(l_a + 1)] \frac{f(r)g(r)}{r^2} \right| a \right\rangle \end{aligned} \quad (\text{A3})$$

and

$$\begin{aligned} \sum_{n_p l_p} (2l_p + 1) \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 (E_p - E_a) \langle a | f(r) | p \rangle \langle p | g(r) | a \rangle \\ = \frac{1}{2} \left\langle a \left| \frac{df}{dr} \frac{dg}{dr} + K(K + 1) \frac{f(r)g(r)}{r^2} \right| a \right\rangle, \end{aligned} \quad (\text{A4})$$

where $f(r)$ and $g(r)$ are any differentiable functions of r . Our proof of these results is based on the fact that the functions $R_a(r)$ and $R_p(r)$ are eigenfunctions of the corresponding radial Hamiltonians, h_a and h_p [29]:

$$h_a R_a(r) = E_a R_a(r), \quad h_p R_p(r) = E_p R_p(r), \quad (\text{A5})$$

with

$$h_a \equiv -\frac{1}{2} \left[\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l_a(l_a + 1)}{r^2} \right] + V(r), \quad (\text{A6a})$$

$$h_p \equiv -\frac{1}{2} \left[\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l_p(l_p + 1)}{r^2} \right] + V(r), \quad (\text{A6b})$$

where $V(r)$ is a one-electron potential. Thus,

$$\begin{aligned} (E_p - E_a) \langle p | g(r) | a \rangle &= \int_0^\infty [h_p R_p^*(r)] g(r) R_a(r) r^2 dr \\ &\quad - \int_0^\infty R_p^*(r) g(r) [h_a R_a(r)] r^2 dr. \end{aligned} \quad (\text{A7})$$

In view of the Hermiticity of the Hamiltonian h_p ,

$$\begin{aligned} (E_p - E_a) \langle p | g(r) | a \rangle &= \int_0^\infty R_p^*(r) [h_p g(r) R_a(r)] r^2 dr \\ &\quad - \int_0^\infty R_p^*(r) g(r) [h_a R_a(r)] r^2 dr. \end{aligned} \quad (\text{A8})$$

Using the completeness of the radial functions $R_p(r)$ then yields Eqs. (A1) and (A3) after a short calculation. We carry out the summation over l_p by making use of the sum rules [30]

$$\begin{aligned} \sum_{j,m} (2j + 1) j(j + 1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}^2 \\ = j_1(j_1 + 1) + j_2(j_2 + 1) + 2m_1 m_2 \end{aligned} \quad (\text{A9})$$

and [13]

$$\sum_{j,m} (2j + 1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}^2 = 1, \quad (\text{A10})$$

here with $m_1 = m_2 = 0$. Equations (A2) and (A4) follow.

APPENDIX B: CALCULATION OF $\delta E_a^{(\text{E})}$

For simplicity, we assume here that the wave vector $\mathbf{k}$ is in the positive z direction and that

$$\hat{\epsilon} = \hat{\epsilon}_1 = -(\hat{\mathbf{x}} + i\hat{\mathbf{y}})/\sqrt{2}, \quad (\text{B1})$$

with $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ being unit vectors in the x and y directions. Then, from Eqs. (27a), (28a), and (36),

$$\begin{aligned} \delta E_a^{(\text{E})} &= \frac{2}{\pi c^3} \int_0^\infty \frac{\omega^3 d\omega}{\exp(\omega/k_B T) - 1} \\ &\quad \times \sum_{n_p l_p} \left[\frac{\mathcal{P}_-(n_a l_a n_p l_p, k)}{\omega_{ap} - \omega} + \frac{\mathcal{P}_+(n_a l_a n_p l_p, k)}{\omega_{ap} + \omega} \right] \end{aligned} \quad (\text{B2})$$

with

$$\begin{aligned} \mathcal{P}_-(n_a l_a n_p l_p, k) &= \int_0^1 d\lambda \int_0^1 d\lambda' \frac{1}{2l_a + 1} \\ &\quad \times \sum_{m_a m_p} \langle n_a l_a m_a | \mathbf{r} \cdot \hat{\epsilon}_1 \exp(i\lambda k z) | n_p l_p m_p \rangle \\ &\quad \times \langle n_p l_p m_p | \mathbf{r} \cdot \hat{\epsilon}_1^* \exp(-i\lambda' k z) | n_a l_a m_a \rangle \end{aligned} \quad (\text{B3a})$$

and

$$\begin{aligned} \mathcal{P}_+(n_a l_a n_p l_p, k) &= \int_0^1 d\lambda \int_0^1 d\lambda' \frac{1}{2l_a + 1} \\ &\times \sum_{m_a m_p} \langle n_a l_a m_a | \mathbf{r} \cdot \hat{\mathbf{e}}_1^* \exp(-i\lambda k z) | n_p l_p m_p \rangle \\ &\times \langle n_p l_p m_p | \mathbf{r} \cdot \hat{\mathbf{e}}_1 \exp(i\lambda' k z) | n_a l_a m_a \rangle. \end{aligned} \quad (\text{B3b})$$

We note that

$$\exp(i\lambda k z) = \sqrt{4\pi} \sum_{\Lambda=0}^{\infty} i^{\Lambda} \sqrt{2\Lambda + 1} j_{\Lambda}(\lambda k r) Y_{\Lambda 0}(\hat{\mathbf{r}}) \quad (\text{B4})$$

where the $j_{\Lambda}(\cdot)$'s are spherical Bessel functions. We also note that $\mathbf{r} \cdot \hat{\mathbf{e}}_1 = (4\pi/3)^{1/2} r Y_{11}(\hat{\mathbf{r}})$ for our choice of polarization

vector, and that

$$\begin{aligned} Y_{11}(\hat{\mathbf{r}}) Y_{\Lambda 0}(\hat{\mathbf{r}}) &= \sum_{K\mu} \sqrt{\frac{3(2\Lambda + 1)(2K + 1)}{4\pi}} \\ &\times \begin{pmatrix} 1 & \Lambda & K \\ 1 & 0 & \mu \end{pmatrix} \begin{pmatrix} 1 & \Lambda & K \\ 0 & 0 & 0 \end{pmatrix} Y_{K\mu}^*(\hat{\mathbf{r}}). \end{aligned} \quad (\text{B5})$$

Combining these results and using the recursion relation satisfied by the spherical Bessel functions leads to the following partial wave expansion for the product $Y_{11}(\hat{\mathbf{r}}) \exp(i\lambda k z)$:

$$\begin{aligned} Y_{11}(\hat{\mathbf{r}}) \exp(i\lambda k z) &= -\sqrt{\frac{3}{2}} \sum_{K=1}^{\infty} i^{K+1} \sqrt{K(K+1)(2K+1)} \frac{j_K(\lambda k r)}{\lambda k r} Y_{K1}(\hat{\mathbf{r}}), \end{aligned} \quad (\text{B6})$$

and similarly for the product $Y_{11}^*(\hat{\mathbf{r}}) \exp(-i\lambda' k z)$. Therefore,

$$\begin{aligned} \mathcal{P}_-(n_a l_a n_p l_p, k) &= -\frac{2\pi}{k^2} \int_0^1 d\lambda \int_0^1 d\lambda' \sum_{KK'} i^{K-K'} \frac{\sqrt{KK'(K+1)(K'+1)(2K+1)(2K'+1)}}{2l_a + 1} \\ &\times \frac{1}{\lambda\lambda'} \langle n_a l_a | j_K(\lambda k r) | n_p l_p \rangle \langle n_p l_p | j_{K'}(\lambda' k r) | n_a l_a \rangle \sum_{m_a m_p} \langle Y_{l_a m_a} | Y_{K1} | Y_{l_p m_p} \rangle \langle Y_{l_p m_p} | Y_{K'-1} | Y_{l_a m_a} \rangle. \end{aligned} \quad (\text{B7})$$

The angular part of the right-hand side reduces to a single term since [13]

$$\sum_{m_a m_p} \begin{pmatrix} l_a & K & l_p \\ -m_a & 1 & m_p \end{pmatrix} \begin{pmatrix} l_p & K' & l_p \\ -m_p & -1 & m_a \end{pmatrix} \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_p & K' & l_p \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{2K+1} \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 \delta_{KK'}. \quad (\text{B8})$$

$\mathcal{P}_+(n_a l_a n_p l_p, k)$ can be calculated in the same way, with the same result,

$$\begin{aligned} \mathcal{P}_+(n_a l_a n_p l_p, k) &= \mathcal{P}_-(n_a l_a n_p l_p, k) = \frac{1}{2k^2} \int_0^1 d\lambda \int_0^1 d\lambda' \sum_{K=1}^{\infty} (2K+1)K(K+1) \\ &\times (2l_p + 1) \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{1}{\lambda\lambda'} \langle n_a l_a | j_K(\lambda k r) | n_p l_p \rangle \langle n_p l_p | j_K(\lambda' k r) | n_a l_a \rangle, \end{aligned} \quad (\text{B9})$$

where $\langle n_a l_a | j_K(\lambda k r) | n_p l_p \rangle$ and $\langle n_p l_p | j_K(\lambda' k r) | n_a l_a \rangle$ are the following radial matrix elements:

$$\langle n_a l_a | j_K(\lambda k r) | n_p l_p \rangle = \int_0^{\infty} R_{n_a l_a}^*(r) j_K(\lambda k r) R_{n_p l_p}(r) r^2 dr, \quad (\text{B10a})$$

$$\langle n_p l_p | j_K(\lambda' k r) | n_a l_a \rangle = \int_0^{\infty} R_{n_p l_p}^*(r) j_K(\lambda' k r) R_{n_a l_a}(r) r^2 dr. \quad (\text{B10b})$$

Expanding the spherical Bessel functions in powers of their argument yields

$$\delta E_a^{(\text{E})} = \sum_{K=1}^{\infty} \sum_{q,q'=0}^{\infty} \delta E_{a,qq'}^{(\text{EK})} \quad (\text{B11})$$

with

$$\delta E_{a,qq'}^{(\text{EK})} = -\frac{(-1)^{q+q'}}{q!q'!} \left(\frac{k_B T}{c} \right)^{2K+2q+2q'+1} \sum_{n_p l_p} (2l_p + 1) \begin{pmatrix} l_a & K & l_p \\ 0 & 0 & 0 \end{pmatrix}^2 F_{Kqq'} \left(\frac{E_p - E_a}{k_B T} \right) \langle n_a l_a | r^{K+2q} | n_p l_p \rangle \langle n_p l_p | r^{K+2q'} | n_a l_a \rangle. \quad (\text{B12})$$

The function $F_{Kqq'}(y)$ is a generalization of the function $F_K(y)$ used in Sec. II: $F_K(y) \equiv F_{K00}(y)$ and

$$F_{Kqq'}(y) = \frac{1}{\pi} \frac{K(K+1)(2K+1)}{2^{q+q'}(K+2q)(2K+2q+1)!!(K+2q')(2K+2q'+1)!!} \text{P.V.} \int_0^\infty \left(\frac{1}{y+x} + \frac{1}{y-x} \right) \frac{x^{2K+2q+2q'+1}}{\exp(x)-1} dx \quad (\text{B13})$$

$$\sim -\frac{2y}{\pi} \frac{K(K+1)(2K+1)(2K+2q+2q'-1)!}{2^{q+q'}(K+2q)(2K+2q+1)!!(K+2q')(2K+2q'+1)!!} \zeta(2K+2q+2q') \quad \text{when } |y| \ll 1. \quad (\text{B14})$$

Replacing $F_{Kqq'}(y)$ by its small- $|y|$ form in Eq. (B12) and using Eq. (A2) then leads to the approximate partial shifts,

$$\delta E_{a,qq'}^{(\text{EK})'} = \frac{1}{\pi} \frac{(-1)^{q+q'}}{q!q'!} \frac{K(K+1)(2K+1)(2K+2q+2q'-1)![(K+2q)(K+2q') + K^2 + K]}{2^{q+q'}(K+2q)(2K+2q+1)!!(K+2q')(2K+2q'+1)!!} \\ \times \zeta(2K+2q+2q') \frac{(k_B T)^{2K+2q+2q'}}{c^{2K+2q+2q'+1}} \langle n_a l_a | r^{2K+2q+2q'-2} | n_a l_a \rangle, \quad (\text{B15})$$

and to the following approximate expression of the full electric multipole shift:

$$\delta E_a^{(\text{E})} \approx \delta E_a^{(\text{E})'} = \sum_{K=1}^{\infty} \sum_{q,q'=0}^{\infty} \delta E_{a,qq'}^{(\text{EK})'}. \quad (\text{B16})$$

Comparing Eq. (12) to Eq. (B12) and Eq. (17) to Eq. (B15) shows that $\delta E_{a,00}^{(\text{EK})} \equiv \delta E_a^{(\text{EK})}$ and $\delta E_{a,00}^{(\text{EK})'} \equiv \delta E_a^{(\text{EK})'}$. The present results thus reproduce the electric multipole shifts of Sec. II when retardation is neglected, as should be the case.

APPENDIX C: CALCULATION OF $\delta E_a^{(\text{P})}$ FOR S STATES

Rather than taking the z axis of the system of coordinates along $\mathbf{k}$, it is more convenient here to take the x axis along $\mathbf{k}$ and set $\hat{\beta} = \hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is a unit vector in the z direction. Then, for s states ($l_a = 0$),

$$\langle a | v_M | p \rangle \langle p | v_M^\dagger | a \rangle = \frac{1}{4} \int_0^1 d\lambda \lambda \int_0^1 d\lambda' \lambda' m_p^2 \langle a | \exp(i\lambda kx) | p \rangle \langle p | \exp(-i\lambda' kx) | a \rangle. \quad (\text{C1})$$

Using the expansion

$$\exp(i\lambda kx) = 4\pi \sum_{\Lambda=0}^{\infty} \sum_{\mu=-\Lambda}^{\Lambda} i^\Lambda j_\Lambda(\lambda kr) Y_{\Lambda\mu}^*(\hat{\mathbf{x}}) Y_{\Lambda\mu}(\hat{\mathbf{r}}) \quad (\text{C2})$$

and integrating over the angles reduces Eq. (C1) to the following form:

$$\langle a | v_M | p \rangle \langle p | v_M^\dagger | a \rangle = 4\pi^2 \int_0^1 d\lambda \lambda \int_0^1 d\lambda' \lambda' m_p^2 |Y_{l_p m_p}(\hat{\mathbf{x}})|^2 \langle n_a l_a | j_{l_p}(\lambda kr) | n_p l_p \rangle \langle n_p l_p | j_{l_p}(\lambda' kr) | l_a n_a \rangle, \quad (\text{C3})$$

and similarly for $\langle a | v_M^\dagger | p \rangle \langle p | v_M | a \rangle$. The summation over intermediate states appearing in Eq. (27b) involves a summation over n_p , a summation over l_p , and a summation over m_p . The latter reduces to summing $m_p^2 |Y_{l_p m_p}(\hat{\mathbf{x}})|^2$ over the possible values of m_p . From general results [31],

$$\sum_{m_p} m_p^2 |Y_{l_p m_p}(\hat{\mathbf{x}})|^2 = \frac{l_p(l_p+1)(2l_p+1)}{8\pi}. \quad (\text{C4})$$

Expanding the spherical Bessel functions in power series, folding $\delta E_a^{(\text{P})}(\mathcal{E}, \mathbf{k}, \hat{\mathbf{e}})$ with the spectral and angular distributions of the BBR radiation, making the small $|E_p - E_a|/(k_B T)$ approximation, and summing over n_p by using Eq. (A1) gives

$$\delta E_a^{(\text{P})} \approx \delta E_a^{(\text{P})'} = \sum_{l_p=0}^{\infty} \sum_{q,q'=0}^{\infty} \frac{1}{4\pi} \frac{(-1)^{q+q'}}{q!q'!} \frac{l_p(l_p+1)(2l_p+1)[(2q+l_p)(2q'+l_p) + l_p(l_p+1)](2q+2q'+2l_p+1)!}{(2l_p+2q+1)!(2l_p+2q'+1)!(2q+l_p+2)(2q'+l_p+2)} \\ \times \zeta(2l_p+2q+2q'+2) \frac{(k_B T)^{2l_p+2q+2q'+2}}{c^{2l_p+2q+2q'+5}} \langle n_a l_a | r^{2l_p+2q+2q'+2} | n_a l_a \rangle. \quad (\text{C5})$$

We stress that this result only applies to the $l_a = 0$ case.

APPENDIX D: CALCULATION OF $\delta E_a^{(\text{D})}$

We take $\mathbf{k}$ to be in the positive z direction and set

$$\hat{\beta} = -i\hat{\mathbf{e}}_1 = (i\hat{\mathbf{x}} - \hat{\mathbf{y}})/\sqrt{2}. \quad (\text{D1})$$

Thus $\mathbf{k} \cdot \mathbf{r} = kz = kr \cos \theta$, where θ is the angle between the vector $\mathbf{r}$ and the positive z axis, and

$$(\mathbf{r} \times \hat{\boldsymbol{\beta}}) \cdot (\mathbf{r} \times \hat{\boldsymbol{\beta}}^*) = \frac{1}{2} r^2 (1 + \cos^2 \theta). \quad (\text{D2})$$

Hence, from Eqs. (27c), (28c), and (36),

$$\delta E_a^{(\text{D})} = \frac{1}{\pi c^5} \int_0^\infty \frac{\omega^3 d\omega}{\exp(\omega/k_B T) - 1} \int_0^1 d\lambda \int_0^1 d\lambda' \frac{\lambda \lambda'}{2l_a + 1} \sum_{m_a} \langle a | r^2 (1 + \cos^2 \theta) \exp[i(\lambda - \lambda') kr \cos \theta] | a \rangle. \quad (\text{D3})$$

Since

$$\cos^2 \theta \exp[i(\lambda - \lambda') kr \cos \theta] = \frac{d}{d\lambda kr} \exp(i\lambda kr \cos \theta) \frac{d}{d\lambda' kr} \exp(-i\lambda' kr \cos \theta), \quad (\text{D4})$$

expanding the exponentials in partial waves yields

$$\begin{aligned} & \sum_{m_a} \langle a | r^2 (1 + \cos^2 \theta) \exp[i(\lambda - \lambda') kr \cos \theta] | a \rangle \\ &= 4\pi \sum_{\Lambda, \Lambda'=0}^\infty i^{\Lambda-\Lambda'} \sqrt{(2\Lambda+1)(2\Lambda'+1)} \langle n_a l_a | r^2 j_\Lambda(\lambda kr) j_{\Lambda'}(\lambda' kr) + r^2 j'_\Lambda(\lambda kr) j'_{\Lambda'}(\lambda' kr) | n_a l_a \rangle \sum_{m_a} \langle Y_{l_a m_a} | Y_{\Lambda 0} Y_{\Lambda' 0} | Y_{l_a m_a} \rangle, \end{aligned} \quad (\text{D5})$$

where $j'_n(\cdot)$ denotes the derivative of the spherical Bessel function $j_n(\cdot)$ with respect to its argument. We calculate the angular matrix element by writing $Y_{l_a m_a}^*(\hat{\mathbf{r}}) Y_{\Lambda 0}(\hat{\mathbf{r}})$ and $Y_{\Lambda' 0}(\hat{\mathbf{r}}) Y_{l_a m_a}(\hat{\mathbf{r}})$ as linear combinations of spherical harmonics, with the result that

$$\begin{aligned} \sum_{m_a} \langle Y_{l_a m_a} | Y_{\Lambda 0} Y_{\Lambda' 0} | Y_{l_a m_a} \rangle &= \sum_{m_a} \sum_{K\mu} \sum_{K'\mu'} (-1)^{m_a+\mu'} (2l_a+1) \frac{\sqrt{(2\Lambda+1)(2K+1)(2\Lambda'+1)(2K'+1)}}{4\pi} \\ &\times \begin{pmatrix} l_a & \Lambda & K \\ -m_a & 0 & \mu \end{pmatrix} \begin{pmatrix} l_a & \Lambda & K \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \Lambda' & l_a & K' \\ 0 & m_a & \mu' \end{pmatrix} \begin{pmatrix} \Lambda' & l_a & K' \\ 0 & 0 & 0 \end{pmatrix} \delta_{KK'} \delta_{\mu-\mu'}. \end{aligned} \quad (\text{D6})$$

Combining Eqs. (D3), (D5), and (D6) then gives

$$\delta E_a^{(\text{D})} = \frac{1}{\pi c^5} \int_0^\infty \frac{\omega^3 d\omega}{\exp(\omega/k_B T) - 1} \int_0^1 d\lambda \int_0^1 d\lambda' \lambda \lambda' \sum_{\Lambda=0}^\infty (2\Lambda+1) \langle n_a l_a | r^2 j_\Lambda(\lambda kr) j_\Lambda(\lambda' kr) + r^2 j'_\Lambda(\lambda kr) j'_\Lambda(\lambda' kr) | n_a l_a \rangle. \quad (\text{D7})$$

Expanding the Bessel functions in power series, replacing k by ω/c , and integrating the result over ω , λ , and λ' reduces the diamagnetic shift to the form of Eq. (45).

-
- [1] S. G. Porsev and A. Derevianko, Multipolar theory of blackbody radiation shift of atomic energy levels and its implications for optical lattice clocks, *Phys. Rev. A* **74**, 020502(R) (2006).
 - [2] B. Arora, D. K. Nandy, and B. K. Sahoo, Multipolar blackbody radiation shifts for single-ion clocks, *Phys. Rev. A* **85**, 012506 (2012).
 - [3] B. K. Sahoo, Role of the multipolar black-body radiation shifts in the atomic clocks at the 10^{-18} uncertainty level, *Pramana* **83**, 255 (2014).
 - [4] Z.-M. Tang, Y.-F. Wei, B. K. Sahoo, C.-B. Li, Y. Yang, Y. Zou, and X.-R. Huang, Blackbody-radiation Zeeman shifts in optical clocks: The role of fine-structure intramanifold resonances, *Phys. Rev. A* **110**, 043108 (2024).
 - [5] J. W. Farley and W. H. Wing, Accurate calculation of dynamic Stark shifts and depopulation rates of Rydberg energy levels induced by blackbody radiation. Hydrogen, helium, and alkali-metal atoms, *Phys. Rev. A* **23**, 2397 (1981).
 - [6] T. A. Zalialiutdinov, A. A. Anikin, and D. A. Soloviev, Thermally induced Stark shifts of highly excited states of hydrogen atom, *J. Exp. Theor. Phys.* **135**, 605 (2022).
 - [7] I. I. Beterov, D. B. Tretyakov, I. I. Ryabtsev, V. M. Endin, A. Ekers, and N. N. Bezuglov, Ionization of Rydberg atoms by blackbody radiation, *New J. Phys.* **11**, 013052 (2009).
 - [8] I. L. Glukhov, A. A. Kamenski, and V. D. Ovsiannikov, The use of photoionization cross section for evaluating contribution of continuum to the blackbody radiation induced shift and broadening of Rydberg-state energy levels of group IIb ions, *J. Quant. Spectrosc. Radiat. Transfer* **280**, 108068 (2022).
 - [9] T. F. Gallagher and W. E. Cooke, Interactions of blackbody radiation with atoms, *Phys. Rev. Lett.* **42**, 835 (1979).
 - [10] K. Beloy, B. D. Hunt, R. C. Brown, T. Bothwell, Y. S. Hassan, J. L. Siegel, T. Grogan, and A. D. Ludlow, Blackbody radiation Zeeman shift in Rydberg atoms, *Phys. Rev. A* **111**, 062819 (2025).
 - [11] J. J. Lopez-Rodriguez, A. Bobylev, P. Kvasov, T. Zalialiutdinov, and D. Solov'yev, Multipole decomposition of the thermal one-loop self-energy correction for a bound atomic electron, *Phys. Rev. A* **112**, 052807 (2025).
 - [12] K. Bockasten, Mean values of powers of the radius for hydrogenic electron orbits, *Phys. Rev. A* **9**, 1087 (1974).

- [13] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, NJ, 1974).
- [14] $\zeta(2) = \pi^2/6$, $\zeta(4) = \pi^4/90$, etc. See, e.g., *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 2013).
- [15] M. P. A. Jones, R. M. Potvliege, and M. Spannowsky, Probing new physics using Rydberg states of atomic hydrogen, *Phys. Rev. Res.* **2**, 013244 (2020).
- [16] The required exact values of the matrix elements of r^k between bound states of hydrogen were calculated using a quadruple precision version of the HYDMATEL program [M. L. Sánchez and A. L. Piñeiro, HYDMATEL: a code to calculate matrix elements for hydrogen-like atoms, *Comput. Phys. Commun.* **75**, 185 (1993)].
- [17] X. Mei, W. Zhou, Z. Zhong, and H. Qiao, Analytical expressions of non-relativistic static multipole polarizabilities for hydrogen-like ions, *Chin. Phys. B* **29**, 043101 (2020).
- [18] R. M. Potvliege (unpublished).
- [19] N. Šibalić, J. D. Pritchard, C. S. Adams, and K. J. Weatherill, ARC: An open-source library for calculating properties of alkali Rydberg atoms, *Comput. Phys. Commun.* **220**, 319 (2017).
- [20] ARC documentation, <https://arc-alkali-rydberg-calculator.readthedocs.io/en/latest/index.html>.
- [21] These multipole shifts decrease rapidly with T , though. For example, the quadrupole frequency shift of the $50s$ state is 1.2 Hz at 300 K but only 5.2 mHz at 77 K. The temperature at which the quadrupole shift is of the order of 1 Hz is approximately proportional to $1/n_a$.
- [22] R. Loudon, *The Quantum Theory of Light*, 2nd ed. (Oxford University, New York, 1983).
- [23] Y. Komninos, T. Mercouris, and C. A. Nicolaides, Theory and computation of the matrix elements of the full interaction of the electromagnetic field with an atomic state: Application to the Rydberg and the continuous spectrum, *Phys. Rev. A* **65**, 043412 (2002).
- [24] R. Anzaki, Y. Shinohara, T. Sato, and K. L. Ishikawa, Gauge invariance beyond the electric dipole approximation, *Phys. Rev. A* **98**, 063410 (2018).
- [25] The Hamiltonian of Eq. (25) is a natural generalization of the familiar length gauge Hamiltonian generally used for calculating BBR shift, which is an advantage of this formulation.
- [26] The values of the coefficients, $a_n^{(E)}$, $b_n^{(E)}$, $a_n^{(P)}$, $b_n^{(P)}$, $a_n^{(D)}$, and $b_n^{(D)}$ for n ranging from 1 to 50 and the data plotted in the figures accompanying this article can be found at <https://researchdata.durham.ac.uk/files/r2tq57nr11w>.
- [27] S. Pasternack, On the mean value of r^s for Keplerian systems, *Proc. Natl. Acad. Sci. USA* **23**, 91 (1937).
- [28] We used Wynn's epsilon algorithm for this Padé summation [P. Wynn, On the convergence and stability of the epsilon algorithm, *SIAM J. Numer. Anal.* **3**, 91 (1966); P. R. Graves-Morris, D. E. Roberts, and A. Salam, The epsilon algorithm and related topics, *J. Comput. Appl. Math.* **122**, 51 (2000)]. In our implementation of this algorithm, the program constructs the diagonal Padé approximants of the series up to order [21/21] in ω^2 , which is high enough to ensure that for increasing order these diagonal elements converge to a stable value within a relative difference of 1 part in 10^{12} or better for all relevant values of ω . We checked that summing the electric and diamagnetic contributions separately or adding them together before summation does not make any significant difference to the final results.
- [29] This approach is similar to one that has been used for deriving other sum rules [R. Jackiw, Quantum-mechanical sum rules, *Phys. Rev.* **157**, 1220 (1967)].
- [30] J.-C. Pain and F. Gilleron, New sum rules for Wigner $3jm$ symbols: Application to expectation values of hydrogenic ions, *J. Phys. B: At. Mol. Opt. Phys.* **54**, 065002 (2021).
- [31] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* (World Scientific, Singapore, 2021).