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Blackbody radiation shift of the B$^+$ clock transition

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A calculation of the blackbody radiation shift of the B$^+$ clock transition is performed. The polarizabilities of the B$^+ 2s^2\ ^1S^e$, $2s2p\ ^1P^o$, and $2s2p\ ^3P^o$ states are computed using the configuration interaction method with an underlying semiempirical core potential. The recommended dipole polarizabilities are $9.64(3)a_0^3$, $7.78(3)a_0^3$ and $16.55(5)a_0^3$, respectively. The derived frequency shift for the $2s^2\ ^1S^e \rightarrow 2s2p\ ^3P^o_0$ transition at 300 K is 0.0160(5) Hz. The dipole polarizabilities agree with an earlier relativistic calculation [Safronova *et al.*, Phys. Rev. Lett. **107**, 143006 (2011)] to better than 0.2%. Quadrupole and octupole polarizabilities and nonadiabatic multipole polarizabilities are also reported.

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I. INTRODUCTION

Recent advances in laser control of atoms and ions have lead to major improvements in the precision of optical frequency standards [1,2]. These improvements are expected to result in a new definition of the second [3]. Indeed, an optical clock using the Al$^+$ ion using quantum logic technology has been developed with a fractional frequency uncertainty of 8.6×10^{-18} [4]. This uncertainty is equivalent to a drift of 1 s in 3.7×10^9 years.

The ultrahigh precision achieved by these optical frequency standards means they are sensitive to very small environmental influences. One of these influences is the blackbody radiation (BBR) emitted by the apparatus in which the atomic or ionic clock is enclosed. This BBR radiation, by means of the ac Stark effect, changes the energies of the two states of the clock transition, and this can alter the frequency of the atomic clock [5,6].

This BBR shift is, in principle, one of the largest sources of systematic error in these clocks [5–11]. The BBR shift (in Hz) can be written as

$$\Delta\nu_{\rm BBR} = 6.579684 \times 10^{15}(\Delta E_{\rm upper} - \Delta E_{\rm lower}), \tag{1}$$

where the electric dipole ($E1$) induced BBR energy shift of an atomic state can be approximately calculated as [12]

$$\Delta E \approx -\tfrac{2}{15}(\alpha\pi)^3\alpha_1(0)T^4\ . \tag{2}$$

The dipole polarizability of the relevant quantum state is α_1, and T is the temperature. Knowledge of the dipole polarizabilities permits a temperature-dependent BBR correction to be made to the clock. The uncertainty in the $E1$ BBR shift can be written as

$$\delta(\Delta\nu_{\rm BBR}) = \Delta\nu_{\rm BBR}\left(\frac{\delta(\Delta\alpha_1)}{\Delta\alpha_1} + \frac{4\delta T}{T}\right). \tag{3}$$

Calculations of the B$^+$ ($2s^2\ ^1S^e_0$–$2s2p\ ^3P^o_0$) clock transition have previously been made [13] using a relativistic configuration interaction (CI) calculation to account for valence correlations while an all-order many-body perturbation theory approach is used to account for core and core-valence correlations. The paper reported the dipole polarizabilities and demonstrated that the clock transition for this ion had a relatively small 300 K BBR shift of 0.0159 Hz [13]. This paper confirms this result and extends the data set for B$^+$ to encompass higher-order polarizabilities. Calculations are performed using the CI method with a semiempirical core-polarization potential to encompass core-valence correlations.

II. METHODOLOGY

The CI calculations used to generate the physical and L^2 pseudostates were similar in style to those used previously to determine the dispersion parameters and polarizabilities of a number of two-electron systems [14–17]. The Hamiltonian for the two active electrons is written as

$$H = \sum_{i=1}^{2}\left(-\frac{1}{2}\nabla_i^2 + V_{\rm dir}(\mathbf{r}_i) + V_{\rm exc}(\mathbf{r}_i) + V_{\rm p1}(\mathbf{r}_i)\right) + V_{\rm p2}(\mathbf{r}_1,\mathbf{r}_2) + \frac{1}{r_{12}}. \tag{4}$$

The direct, $V_{\rm dir}$, and exchange, $V_{\rm exc}$, interactions of the valence electrons with the Hartree-Fock (HF) core were calculated exactly. The $1s^2$ core wave function was taken from a HF calculation of the B^{2+} ground state using a Slater-type orbital (STO) basis. The ℓ-dependent polarization potential $V_{\rm p1}$ was semiempirical in nature, with the functional form

$$V_{\rm p1}(\mathbf{r}) = -\sum_{\ell m}\frac{\alpha_{\rm core}g_\ell^2(r)}{2r^4}|\ell m\rangle\langle\ell m|. \tag{5}$$

The coefficient $\alpha_{\rm core}$ is the static dipole polarizability of the core, and $g_\ell^2(r) = 1 - \exp\left(-r^6/\rho_\ell^6\right)$ is a cutoff function designed to make the polarization potential finite at the origin. The cutoff parameters ρ_ℓ were tuned to reproduce the binding energies of the B^{2+} ns ground state and the np, nd, and nf excited states. The core polarizability was chosen to be $\alpha_{\rm core} = 0.019644a_0^3$ [18,19]. The cutoff parameters for $\ell = 0 \rightarrow 3$ were 0.6835, 0.6899, 0.8874, and 2.945 a_0 respectively.

To get more accurate energy levels and polarizabilities, it is essential to include a two-body polarization term V_{p2} in the Hamiltonian. The polarization of the core by one electron is influenced by the presence of the second valence electron. Omission of the two-body term would typically result in a

$2s^2$ state that would be too tightly bound. A discussion of the importance of the two-body polarization potential can be found in Ref. [20]. The two-body polarization potential is adopted in the present calculation with the form

$$V_{\mathrm{p2}}(\mathbf{r}_i,\mathbf{r}_j) = -\frac{\alpha_d}{r_i^3 r_j^3}(\mathbf{r}_i \cdot \mathbf{r}_j) g_{\mathrm{p2}}(r_i) g_{\mathrm{p2}}(r_j), \qquad (6)$$

where g_{p2} has the same functional form as $g_\ell(r)$. The cutoff parameter for $g_{\mathrm{p2}}(r)$ was chosen as $0.6867a_0$, the average of ρ_0 and ρ_1 (the ρ_2 and ρ_3 cutoff parameters are influenced by finite nuclear mass effects, and thus they were not used in determining the cutoff parameter for V_{p2}). Use of $0.6867a_0$ for the two-body cutoff parameter resulted in energies that were close to the experimental binding energies for most of the lowest-lying states of B^+. Some small adjustments to the ρ_ℓ, described later, were made later to further improve agreement with the experimental B^+ spectrum. The approach to solve the Schrödinger equation is termed a configuration interaction plus core polarization (CICP).

There were a total of 163 valence orbitals with a maximum orbital angular momentum of $\ell = 5$. The radial dependence of the orbitals were described by a mixture of STOs and Laguerre-type orbitals (LTOs) [14]. The number of active orbitals for $\ell = 0 \to 5$ were 32, 32, 30, 25, 25, and 19, respectively. Some $\ell = 0$ valence orbitals were generated from the STOs used for the core. All the other orbitals were written as LTOs due to their superior linear dependence properties when compared with STO basis sets. The use of the large orbital basis resulted in wave functions and energies for the low-lying states that were close to convergence.

The length of the CI expansions for the different states of B^+ ranged from 2000 to 5000. Some small changes were made to the ρ_ℓ values that were originally tuned to the B^{2+} spectrum to improve the agreement of the B^+ energies with experiment. The oscillator strengths were computed with operators that included polarization corrections [14,21,22]. The cutoff parameter in the polarization correction to dipole operator was $0.6867a_0$.

III. RESULTS AND DISCUSSION

A. Energy levels

The energy levels of the present calculations are given in Table I and compared with experiment. The biggest discrepancy for the B^{2+} ion was 10^{-4} a.u. The cutoff parameters of the polarization potential were tuned to reproduce the experimental binding energies of the lowest states of each symmetry.

Small adjustments to the cutoff parameters were made for the calculations of the B^+ states. For example, the value of ρ_0 was reset to $0.7064a_0$ for the calculation of the states of the ${}^1S^e$ symmetry. The value of ρ_0 was fixed by requiring that the theoretical and experimental energies for the $2s^2$ state be the same. Other fine-tunings of the cutoff parameters were made for all symmetries. The biggest discrepancy between theoretical and experimental energies occurs for the ${}^1S^e$ symmetry and is only 2×10^{-4} a.u. The agreement between the theoretical and experimental energy levels is sufficiently close to discount the possibility that energy-level considerations might make a significant contribution to the uncertainty in the radial matrix elements.

TABLE I. Theoretical and experimental energy levels (in hartrees) for some of the low-lying states of the B^+ and B^{2+} ions. The energies are given relative to the energy of the B^{3+} core. The experimental energies for the multiplet states are averages with the usual $(2J+1)$ weighting factors. The experimental data were taken from the National Institute of Standards and Technology [23].

State	Present	Experiment
	B^{2+}	
$2s\ {}^2S^e$	−1.393924	−1.393924
$2p\ {}^2P^o$	−1.173483	−1.173483
$3s\ {}^2S^e$	−0.572792	−0.572863
$3p\ {}^2P^o$	−0.514642	−0.514743
$3d\ {}^2D^e$	−0.500561	−0.500561
$4s\ {}^2S^e$	−0.310856	−0.310891
$4p\ {}^2P^o$	−0.287444	−0.287498
$4d\ {}^2D^e$	−0.281527	−0.281529
$4f\ {}^2F^o$	−0.281269	−0.281269
	B^+	
$2s^2\ {}^1S^e$	−2.318347	−2.318347
$2s2p\ {}^3P^o$	−2.148168	−2.148168
$2s2p\ {}^1P^o$	−1.983927	−1.983927
$2p^2\ {}^3P^e$	−1.867605	−1.867605
$2p^2\ {}^1D^e$	−1.851947	−1.851947
$2p^2\ {}^1S^e$	−1.736606	−1.736679
$2s3s\ {}^3S^e$	−1.727053	−1.727053
$2s3s\ {}^1S^e$	−1.691092	−1.691293
$2s3p\ {}^3P^o$	−1.662237	−1.662269
$2s3p\ {}^1P^o$	−1.661828	−1.661765
$2s3d\ {}^3D^e$	−1.631961	−1.631961
$2s3d\ {}^1D^e$	−1.613484	−1.613545

B. Oscillator strengths of low-lying transitions

The oscillator strengths for the transitions between the low manifold states are listed in Table II. The absorption oscillator strength from state ψ_i to state ψ_j is calculated according to the identity [14,44]

$$f_{ij}^{(k)} = \frac{2|\langle \psi_i; L_i \parallel r^k \mathbf{C}^k(\hat{\mathbf{r}}) \parallel \psi_j; L_j \rangle|^2 \epsilon_{ji}}{(2k+1)(2L_i+1)} . \qquad (7)$$

In this expression, $\epsilon_{ji} = (E_j - E_i)$ is the energy difference between the initial state and final state, k is the multipolarity of the transition, and $\mathbf{C}^k(\hat{\mathbf{r}})$ is a spherical tensor. Experimental energy differences were used for the calculation of oscillator strengths.

There have been many calculations performed for the energy levels and oscillator strengths for B^{2+} [24–26,28,45,46] and B^+ [29–33,35–38,40,43,47–51]. Not all of the theoretical calculations were tabulated. Table II gives the reported results of the calculations that are deemed to be the most accurate or of particular relevance to present calculations.

For the B^{2+} ion f values are given the multiconfiguration Hartree-Fock calculation with Briet-Pauli corrections (MCHF-BP) [24]. The present calculations agree with the MCHF-BP values to an accuracy of 0.0001. While the present calculations are ostensibly nonrelativistic, they implicitly

TABLE II. Absorption oscillator strengths for various dipole transition lines of the B^+ and B^{2+} ions. The experimental energy differences were used in the calculation of the CICP oscillator strengths.

Transition	CICP	BCICP	MCHF-BP	MCHF	CI	Other theory	Experiment
				B^{2+}			
$2s\to 2p$	0.36360		0.36370 [24]		0.36389 [25]	0.363243[a] [26]	0.35(2) [27]
$2s\to 3p$	0.15333		0.15346 [24]		0.15376 [28]		0.15(1) [27]
$2s\to 4p$	0.04969				0.04981 [28]		
$2p\to 3s$	0.04640		0.04636 [24]				0.05(1) [27]
$2p\to 3d$	0.63801		0.63803 [24]				0.62(6) [27]
				B^+			
$2s^2\ {}^1S^e\to 2s2p\ {}^1P^o$	0.99907	1.002 [29]	1.001 [30]	0.9976(22) [31] 0.999(5) [35]	0.9997 [32] 1.005 [36] 0.9998[d] [38] 1.0028[e] [13]	1.0012[b] [33] 1.0012[c] [37]	0.98(8) [34] 0.71(5) [27] 0.98(6) [39]
$2s^2\ {}^1S^e\to 2s3p\ {}^1P^o$	0.10959	0.108 [29]	0.1087 [30]	0.1093(3) [40]			
$2s2p\ {}^1P^o\to 2p^2\ {}^1D^e$	0.16195	0.162 [29]	0.1621 [30]	0.1608(44) [31]	0.1625 [32]		0.192(9) [41] 0.114(6) [42]
$2s2p\ {}^1P^o\to 2s3d\ {}^1D^e$	0.51545	0.514 [29]	0.5161 [30]		0.5199 [32]		0.49(2) [27]
$2s2p\ {}^1P^o\to 2p^2\ {}^1S^e$	0.22591	0.227 [29]	0.2259 [30]	0.2257(38) [31]	0.2264 [32]		0.24(2) [34] 0.20(1) [27] 0.163(11) [41]
$2s2p\ {}^1P^o\to 2s3s\ {}^1S^e$	0.00008		0.00019 [30]		0.00007 [32]		0.039(2) [27]
$2s2p\ {}^3P^o\to 2p^2\ {}^3P^e$	0.34298	0.365 [43]	0.34292 [30]	0.3427(2) [31]	0.3427 [32]		0.34(3) [34] 0.32(2) [27]
$2s2p\ {}^3P^o\to 2s3s\ {}^3S^e$	0.06377		0.06401 [30]				
$2s2p\ {}^3P^o\to 2s3d\ {}^3D^e$	0.47627	0.473 [29]	0.47597 [30]				0.49(2) [27]
$2p2p\ {}^3P^e\to 2p3d\ {}^3D^o$	0.62300	0.310 [43]					

[a] Hylleraas-type variational method.

[b] Multiconfiguration Dirac-Fock (MCDF) method.

[c] Relativistic MBPT calculation.

[d] Relativistic CI calculation with MBPT theory.

[e] Relativistic CI calculation with all order MBPT theory. Calculated with theoretical energy differences.

include relativistic corrections since the energies are tuned to experimental values. The $2s\to 2p$ oscillator strength computed with the Hylleraas method [26] is close to the nonrelativistic limit, but the Hylleraas calculation omits any relativistic effects, and the Hylleraas energy difference for the $2s\to 2p$ transitions is 0.22016 a.u., which is about 0.1% smaller than the experimental energy difference. The full core plus correlation calculation [25,28,45] listed in the CI column is a variant of the configuration interaction approach.

There is one previous calculation for B^+ that is very similar in concept to the present methodology. That was a CI calculation with a semiempirical core potential [29,43]. The major distinction was the adoption of a B-spline basis, so this calculation is abbreviated as BCICP in Table II. With a few exceptions, the CICP and BCICP oscillator strengths agree to about 1%. When the BCICP oscillator strengths are different from the present values, one also finds the BCICP oscillator strengths also disagreeing with the MCHF-BP B^{2+} oscillator strengths [30].

There is also better than 0.3% agreement of the CICP calculation with MCHF oscillator strengths with two exceptions. The MCHF oscillator strength [31] for the $2s2p\ {}^1P^o \to 2p^2\ {}^1D^e$ transition is about 1% smaller than the CICP oscillator strength. The MCHF oscillator strength, however, is about 1% smaller than the BCICP and MCHF-BP oscillator strengths. There is also agreement at better than 1% level with a CI calculation [32] except for the case of the $2s2p\ {}^1P^o\to 2s3s\ {}^1S^e$ transition, which has a very small oscillator strength.

There have been two calculations which combine relativistic CI calculations with many-body perturbation theory (CI + MBPT) to represent the core-valence interaction [13,38]. These only gave the oscillator strength for the $2s^2\ {}^1S^e$ to $2s2p\ {}^1P^o$ transition. The total range between the CICP oscillator strengths and two CI + MBPT oscillator strengths is less than 0.4%. The agreement of the CICP oscillator strengths with another two relativistic calculations, which are the MCDF calculation of [33] and the MBPT calculation of [37], is also at 0.2% level.

Some experimental oscillator strength measurements [27,34,39,41,42] are also listed in Table II for completeness. The precision of the experimental data is not as high as many of the theoretical oscillator strengths.

C. Scalar and tensor polarizabilities

This analysis is done under the premise that spin-orbit effects are small and the radial parts of the wave functions are the same for the states with different J. All the polarization parameters reported here are calculated using their respective oscillator strength sum rules. The multipole oscillator strengths

$f_{ij}^{(k)}$ are defined in Eq. (7). Then the adiabatic multipole polarizabilities α_k from state i are written as [52]

$$\alpha_k = \sum_j \frac{f_{ij}^{(k)}}{\epsilon_{ji}^2}. \tag{8}$$

Related sum rules, such as the nonadiabatic multipole polarizability β_k and $S_k(-4)$, are given as [14]

$$\beta_k = \frac{1}{2}\sum_j \frac{f_{ij}^{(k)}}{\epsilon_{ji}^3} \tag{9}$$

and [5]

$$S_k(-4) = \sum_j \frac{f_{ij}^{(k)}}{\epsilon_{ji}^4}. \tag{10}$$

The $S_k(-4)$ sum rule gives the lowest-order frequency-dependent component to the dynamic polarizability through the relation

$$\alpha_k(\omega) = \alpha_k(0) + \omega^2 S_k(-4) + \cdots . \tag{11}$$

States with a nonzero angular momentum will also have a tensor polarizability [5,53]. For a state with angular momentum L_0 (J_0), this is defined as the polarizability of the magnetic sublevel with $M = L_0$ ($M = J_0$). The total polarizability is written in terms of both a scalar and a tensor polarizability. The scalar polarizability represents the average shift of the different M levels while the tensor polarizability gives the differential shift.

This tensor polarizability can be expressed in terms of f-value sum rules. For an $L_0 = 1$ initial state, one can write the tensor polarizability for a dipole field as [5]

$$\alpha_{2,L_0L_0} = -\left(\sum_{n,L_n=0} \frac{f_{0n}}{\epsilon_{n0}^2} - \frac{1}{2}\sum_{n,L_n=1} \frac{f_{0n}}{\epsilon_{n0}^2} + \frac{1}{10}\sum_{n,L_n=2} \frac{f_{0n}}{\epsilon_{n0}^2}\right). \tag{12}$$

If the initial state is a $L_0 = 2$ state, one can use the expressions in Eq. [53] and get the f-value sum

$$\alpha_{2,L_0L_0} = -\left(\sum_{n,L_n=1} \frac{f_{0n}}{\epsilon_{n0}^2} - \sum_{n,L_n=2} \frac{f_{0n}}{\epsilon_{n0}^2} + \frac{2}{7}\sum_{n,L_n=3} \frac{f_{0n}}{\epsilon_{n0}^2}\right). \tag{13}$$

The core does not make a contribution to the tensor polarizability since it has an equal impact on all the different M levels.

The development above is for LS coupled states, but it is common to give the tensor polarizability for LSJ states. These can be related to the LS states by geometric factors arising from the application of Racah algebra. The scalar polarizabilities for the different J levels are the same (if spin-orbit splitting is neglected) and equal to the scalar polarizability in the L representation. The tensor polarizabilities between the L and J representations can be related using the expressions of [53]. When $L_0 = 1$ and $J_0 = 0$, one finds $\alpha_{2,J_0J_0} = 0$ while the $J_0 = 1$ case gives $\alpha_{2,J_0J_0} = -\frac{1}{2}\alpha_{2,L_0L_0}$.

TABLE III. The pseudo-oscillator strength distribution for the core B^{3+}. The energy shift parameter ϵ_i and the adiabatic (α_{core}) and nonadiabatic (β_{core}) core polarizabilities from Hylleraas calculations [18] are also displayed. The numbers in the square brackets denote powers of 10.

	ϵ_i	$f_i^{(k)}$	α_{core}	β_{core}
Dipole	−16.67592	1.0	1.9644[−2]	1.1243[−3]
	−7.89382	1.0		
Quadrupole	−21.91592	0.28537	3.4266[−3]	1.5237[−4]
	−10.14212	0.28537		
Octupole	−22.51592	0.15844	1.5216[−3]	5.9751[−5]
	−11.44722	0.15844		

1. Core polarizabilities

The energy distribution of the oscillator strengths originating from core excitations was estimated using a semiempirical technique [14]. This approach utilizes f-value sum rules to construct the pseudo-oscillator strength distributions,

$$\alpha_{k,\text{core}} = \sum_{i\in\text{core}} \frac{kN_i\langle r_i^{2k-2}\rangle}{(\epsilon_i)^2}\ , \tag{14}$$

where N_i is the number of electrons in a core orbital and ϵ_i is an energy shift parameter. The energy shift parameter was chosen so that Eq. (14) reproduces accurate estimates of the adiabatic and nonadiabatic core polarizabilities determined by close to exact calculations for dipole, quadrupole, and octupole transitions [18].

The present calculated pseudo-oscillator strength distributions are given in Table III. They can be used in the determination of the dynamic polarizabilities and the long-range van der Waals coefficients of the B^{2+} and B^{+} ions with other atoms.

2. The B^{+} and B^{2+} polarizabilities

Tables IV and V give the scalar adiabatic multipole polarizabilities of the lowest five states of the B^{2+} ion and the lowest three states of the B^{+} ion. The tensor polarizabilities and nonadiabatic polarizabilities as well as the related sum rules $S_k(-4)$ of some states are also listed. The energies of

TABLE IV. The polarizabilities of some low-lying states of the B^{2+} ion. The scalar adiabatic polarizabilities α_k are listed along with some nonadiabatic (β_k) and tensor ($\alpha^{(1)}_{2,L_0L_0}$) polarizabilities. All the polarizabilities are calculated using the experimental energies. The dipole polarizabilities from accurate CI calculations [25,54] are displayed for comparison. The polarizabilities are in atomic units.

State	α_1	β_1	$\alpha^{(1)}_{2,L_0L_0}$	α_2	β_2	α_3
2s $^2S^e$	7.8460	17.137		7.0963	3.8719	30.181
	7.847 [25]					
	7.85 [54]					
$2p\ ^2P^o$	−0.56938	6.9896	2.1659	5.6105	3.1396	48.761
$3s\ ^2S^e$	182.94	1558.1		1539.0	9096.2	14598
$3p\ ^2P^o$	312.04	13153	20.605	643.82	1374.8	65846
$3d\ ^2D^e$	−191.26	7616.0	208.16	10.437	2170.3	−24466

TABLE V. The polarizabilities of the lowest three states of the B$^+$ ion. The scalar adiabatic polarizabilities α_k are listed along with some nonadiabatic (β_k) and tensor ($\alpha^{(1)}_{2,L_0L_0}$) polarizabilities. Values for sum rules $S_1(-4)$ are also presented. All these values are calculated using the experimental energies. The dipole polarizabilities from the relativistic calculation of [13] are displayed for comparison. All polarizabilities are in atomic units.

State	α_1	$S_1(-4)$	β_1	$\alpha^{(1)}_{2,L_0L_0}$	α_2	β_2	α_3
$2s^2\ ^1S^e$	9.6442	80.891	13.757		27.138	20.631	147.01
	9.624 CI + all [13]						
$2s2p\ ^3P^o$	7.7798	66.320	10.737	1.4613	25.011	17.940	220.98
	7.772 CI + all [13]						
$2s2p\ ^1P^o$	16.554	603.57	54.587	−2.1960	44.757	44.266	541.44

the lowest-lying states (i.e., those in Table I) were adjusted to be the same as the experimental energies for the polarizability calculations.

The present CICP dipole polarizability for the B^{2+} ground state is slightly smaller than the polarizability of two very accurate CI-type calculations [25,54]. The differences do not exceed $0.004a_0^3$. The CI calculations are nonrelativistic and are expected to be slightly larger than the actual polarizability [55]. A comparison for the isoelectronic ion Be$^+$ can be used to estimate an uncertainty in the B^{2+} $2s$ states dipole polarizability. A previous CICP calculation gave a dipole polarizability of $24.493a_0^3$, which is very close to the recommended value of $24.489(4)a_0^3$ [55]. Assigning an uncertainty of 0.1% to the B^{2+} ground-state polarizability would seem to be justified. The uncertainties in the polarizabilities for the excited states are expected to be of the same order as that of the ground state except for the case of the $2p$ state, where considerable cancellations occur in the oscillator strength sum rule.

Table V gives the polarizabilities of the B$^+$ states. The only other calculation of the polarizabilities for these states is a recent CI + MBPT calculation [13]. The CI + MBPT calculation gave a polarizability for the $2s^2\ ^1S^e$ ground state that is 0.2% smaller than the present CICP calculation. The difference for the $2s2p\ ^3P^o$ state is 0.1%.

A rough estimate of the uncertainties in the B$^+$ polarizabilities is possible by reference to similar calculations for the Si^{2+} ground state [16]. A CICP calculation gave $11.688a_0^3$, a revised analysis of a resonant excitation Stark ionization spectroscopy (RESIS) experiment gave $11.669a_0^3$ [16,56], and a CI + MBPT calculation gave $11.670(13)a_0^3$ [57]. The comparison between the RESIS and the CICP polarizabilities suggested that a conservative estimate of the ground-state $3s^2\ ^1S^e$ polarizability was 0.25%, while that for the excited states was 0.5%.

Comparisons for Al$^+$ between CICP polarizabilities [17] and CI + MBPT calculations [13] reveal differences between the two calculations that do not exceed 0.4%. The CI + MBPT calculation uses theoretical differences in the calculation of the Al$^+$ polarizabilities and overestimates the $3s^2\ ^1S^e$–$3s3p\ ^3P^o_0$ energy difference by 0.14%. The replacement of the theoretical energy differences by the experimental energy differences would reduce the difference between the CICP and CI + MBPT calculation to less than 0.3%. The analysis for the Al$^+$ system suggests that an uncertainty of 0.3% should be assigned to the polarizability of the $2s^2\ ^1S^e$ state. So the final recommended $2s^2\ ^1S^e$ dipole polarizability is $9.64(3)a_0^3$. Assuming the $2s2p\ ^3p^o_0$ state has the same uncertainty, the final CICP dipole polarizability is $7.78(3)a_0^3$. The scalar dipole polarizability for the $2s2p\ ^1P^o$ state was $16.55(5)a_0^3$, assuming the same relative uncertainty.

Table VI gives a breakdown of the different contributions to the $2s^2\ ^1S^e$, $2s2p\ ^3P^o_0$, and $2s2p\ ^1P^o$ dipole polarizabilities. About 90% of the $2s^2\ ^1S^e$ polarizability comes from the resonant transition, and much of the difference with the CI + MBPT calculation comes from this transition, with the CI + MBPT calculation giving $8.918a_0^3$ [13]. The CI + MBPT calculation overestimated the $2s^2\ ^1S^e$–$2s2p\ ^1P^o$ transition energy difference by 0.27%, so it is possible that part of the discrepancy with the CI + MBPT calculation could be removed by using the experimental energy difference when calculating the polarizability of the resonant transition. It

TABLE VI. Breakdown of the contributions to the dipole polarizabilities of the B$^+$ clock transition states. The $\delta\alpha_1$ column gives the contribution from the indicated transition class. The $\sum\alpha_1$ column gives the accumulated sum. The final polarizabilities are given in boldface.

Transition(s)	$\delta\alpha_1$	$\sum\alpha_1$
	$2s^2\ ^1S^e$ state	
$2s^2\ ^1S^e \to 2s2p\ ^1P^o$	8.9333	8.9333
$2s^2\ ^1S^e \to 2s3p\ ^1P^o$	0.2542	9.1875
$2s^2\ ^1S^e \to nP\ ^1P^o$	0.4370	9.6245
Core	0.01964	**9.6441**
	$2s2p\ ^3P^o_0$ state	
$2s2p\ ^3P^o \to 2s3s\ ^3S^e$	0.3596	0.3596
$2s2p\ ^3P^o \to nS\ ^3S^e$	0.1093	0.4689
$2s2p\ ^3P^o \to 2p^2\ ^3P^e$	4.3573	4.8262
$2s2p\ ^3P^o \to nP\ ^3P^e$	0.0750	4.9012
$2s2p\ ^3P^o \to 2s3d\ ^3D^e$	1.7873	6.6885
$2s2p\ ^3P^o \to nD\ ^3D^e$	1.0717	7.7602
Core	0.01964	**7.7798**
	$2s2p\ ^1P^o$ state	
$2s2p\ ^1P^o \to 2s^2\ ^1S^e$	−2.9778	−2.9778
$2s2p\ ^1P^o \to 2p^2\ ^1S^e$	3.6955	0.7177
$2s2p\ ^1P^o \to nS\ ^1S^e$	0.0707	0.7884
$2s2p\ ^1P^o \to 2p^2\ ^1D^e$	9.2975	10.0859
$2s2p\ ^1P^o \to 2s3d\ ^1D^e$	3.7574	13.8433
$2s2p\ ^1P^o \to nD\ ^1D^e$	2.4125	16.2558
$2s2p\ ^1P^o \to 2p3p\ ^1P^e$	0.1613	16.4171
$2s2p\ ^1P^o \to nP\ ^1P^e$	0.1169	16.5340
Core	0.01964	**16.5536**

should be noted that experimental energy differences were used in a recent CI + MBPT calculation of the polarizability of the $3s^2$ state of Si^{2+} [57].

The present CICP calculation of the ground-state polarizability does not take into consideration the contribution from the $2s^2\ {}^1S^e \rightarrow 2s2p\ {}^3P_1^o$ transition. The oscillator strength for this transition is only 3.361×10^{-8} [30], so this transition can be safely omitted from the determination of the polarizability. This also justifies the omission of the spin-orbit interaction from the effective Hamiltonian for the valence electrons.

D. The BBR shift

The blackbody radiation shift of an atomic clock transition can be approximately calculated using Eqs. (1) and (2). In this expression the temperature (in K) is multiplied by 3.1668153×10^{-6}. Using the present polarizabilities and converting to frequency shifts at 300 K gives $\Delta\nu_{2s^2\,{}^1S^e} = -0.08305$ Hz and $\Delta\nu_{2s2p\,{}^3P_0^o} = -0.06699$ Hz. In the present CICP calculation the dipole polarizability difference for the $2s^2\ {}^1S^e \rightarrow 2s2p\ {}^3P_0^o$ clock transition is $\Delta\alpha_1 = -1.8643a_0^3$. The relativistic CI + MBPT calculation [13] gave $\Delta\alpha_1 = -1.851a_0^3$.

Using a value of $\Delta\alpha_1 = -1.8643a_0^3$ leads to a net frequency shift at 300 K of $\Delta\nu = 0.01605$ Hz. This is consistent with the CI + MBPT result $\Delta\nu = 0.0159(16)$ Hz [13]. A small correction to the polarizabilities needs to be made to allow for the slight variation of the polarizabilities due to the finite temperature of the BBR radiation field,

$$\alpha_1(T) = \alpha_1(1+\eta), \tag{15}$$

where $\alpha_1(T)$ is the polarizability after correction. η is the dynamic correction factor. The leading-order term of η is given by [12]

$$\eta \approx -\frac{40\pi^2 T^2}{21\alpha_1(0)} S_1(-4)\,. \tag{16}$$

The value of η was found to be quite small. In the present CICP calculation, it was -1.42×10^{-4} for the $2s^2\ {}^1S^e$ state and -1.45×10^{-4} for the $2s2p\ {}^3P_0^o$ state. Taking this correction into account, the 300 K dipole polarizabilities of the $2s^2\ {}^1S^e$ state and the $2s2p\ {}^3P^o$ state are $9.6428a_0^3$ and $7.7787a_0^3$, respectively. The polarizability difference is $\Delta\alpha_1 = -1.8642a_0^3$. This is only $0.0001a_0^3$ smaller than the $T = 0$ K value of $-1.8643a_0^3$. It is evident that the effect of the dynamic correction in the B^+ $2s^2\ {}^1S^e \rightarrow 2s2p\ {}^3P_0^o$ clock transition is minuscule.

When the uncertainties in the polarizabilities are taken into consideration, the final recommended CICP polarizability difference at 300 K is $-1.86(6)a_0^3$. The derived frequency shift is 0.0160(5) Hz. The CI + MBPT calculation gave a polarizability difference of $-1.85(18)a_0^3$ and a frequency shift of 0.0159(16) Hz. The difference between the CICP and CI + MBPT calculations of the frequency shift is less than 1.0%.

The uncertainty associated with the CI + MBPT calculation is more than three times larger than that quoted for the present CICP calculation. Although uncertainties are not assigned to the CI + MBPT polarizabilities, their final BBR shift uncertainty indicates uncertainties in their polarizabilities of 1.0%. The CI + MBPT uncertainty estimates seem very conservative given the $0.02a_0^3$ level of agreement between the CICP and CI + MBPT polarizabilities. A more recent CI + MBPT calculation of the polarizability of the Si^{2+} ground state quoted an uncertainty of 0.12% [57].

IV. CONCLUSIONS

The polarizabilities of some low-lying states of the B^{2+} and B^+ ions are computed with large-basis CI calculations with an underlying semiempirical Hamiltonian. The motivation for these calculations was an independent calculation of the BBR shift of the B^+ $2s^2\ {}^1S^e \rightarrow 2s2p\ {}^3P_0^o$ clock transition [13].

The final estimate of the frequency shift, namely, 0.0160(5) Hz, is within 1% of the earlier CI + MBPT calculations [13]. The almost-perfect agreement between these two completely independent calculations gives increased confidence in the respective reliabilities of both calculations. One reason for the good agreement between both calculations is that both calculations give very accurate solutions of the Schrödinger equation with respect to their underlying Hamiltonian. Both the CICP and CI + MBPT approximate the aspects of the physics and, in particular, the core-valence interaction. The CICP calculation uses a HF plus semiempirical polarization potential to simulate core-valence correlation effects. The CI + MBPT calculation uses MBPT to incorporate the dynamical effects going beyond the HF interaction. Making these approximations simplifies the calculation sufficiently to allow a close to numerically exact solution of the Schrödinger equation for the two valence electrons.

In addition to the dipole polarizabilities, the present model computes the quadrupole, octupole, and nonadiabatic dipole polarizabilities. One way to measure the B^+ polarizability would be the RESIS technique [58,59]. The analysis of the raw experimental RESIS data can be improved if estimates of the quadrupole and nonadiabatic dipole polarizability are available.

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