Convergence of the Breit interaction in self-consistent and configuration-interaction approaches

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Much discussion in relativistic atomic physics and quantum optics has related to the interaction of gauge and perturbation of the Hamiltonian or Dirac operator. It has been commented that Lorentz and gauge independence requires different forms of the perturbation operator in shifting from one gauge to another. Equally, it has been commented that gauge convergence is not possible without different operator forms in different bases and without the operator being embedded within the self-consistent kernel. We explore the logic and self-consistency of these arguments, applied to the well-known Breit operator in an area of continuing discussion. We find that convergence is now possible to a remarkable degree including a Breit interaction operator in a form consistent with the gauge for length and velocity relativistic forms of the multipole operator, implemented at the configuration-interaction level. Excellent convergence is obtained for Breit interaction energies, interaction mixing coefficients, interaction transition probabilities and eigenenergies and transition probabilities in complex open shells (transition metal K α transitions and shake satellites), and forbidden transitions.

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I. INTRODUCTION

Relativistic quantum mechanics has been a powerhouse and mainstay for the development of science since Dirac and Sommerfeld. As a cornerstone of atomic physics it has led via quantum electrodynamics to one of the two beautiful theories of our natural world [1]. Recently, this has gained dramatic recognition in small-molecule inorganic theoretical and quantum chemistry as a tool for molecular dynamics. Transition energies, probabilities, and profiles have been predicted with outstanding accuracy, especially for the hydrogen atom [2–4].

In the VUV and x-ray regimes the dominant bound-bound transitions are the characteristic inner-shell transitions of $K\alpha$ and $K\beta$ for $1s-2p$ and $1s-3p$ transitions. Not only are these the most recognizable features of the spectra, but also they evince complex questions of relativistic quantum mechanics which remain unresolved to date. If we begin with the Dirac operator, we recognize early on that the three-body problem of a helium nucleus with two electrons is a formidable challenge and that a neutral or singly ionized system of medium atomic number is an immense challenge to theoretical computation. High-accuracy experimental data are a starting point, but complex shake processes and transition probabilities lead to the need for multiconfigurational Dirac-Hartree-Fock (MCDHF) approaches to begin to address the interesting complexity of the spectra, which, in a nonrelativistic perspective, can be represented by two diagram lines ($K\alpha_1$ and $K\alpha_2$) at a ratio of 2:1. Not so in reality.

At the heart of the problem is the determination to convergence and self-consistency of perhaps 1000 to 200 000 configuration state functions (CSFs), the effective and exchange potentials, and the treatment of correlations within that framework. This has been a target of many people for many years, including I. P. Grant, C. Froese-Fischer, P. Jonsson, and the GRASP atomic code package; for two-electron systems it has been a particular concern of groups such as those of G. W. F. Drake. Despite the long-standing need to understand these transitions, due to the difficulty of atomic structure calculations in complex atoms we have only recently been able to properly investigate these processes theoretically, taking into account such effects as relativity and electron-electron correlation [5,6]. For complex, open-shell atoms, these calculations are discrepant from experiment by up to an order of magnitude. For example, Anagnostopoulos found that the $3p$ satellite contributes 15% to the scandium $K\alpha$ spectrum, compared to Kochur's *ab initio* calculation of 6.0% [7], and Mukoyama's 7.8% [8]. The $3d$ satellite was found experimentally to contribute 38%, compared to the 5.0% predicted by the two previous sources. At present it is not clear whether the theoretical values or the experimental analysis needs further work, but a reasonable expectation is that both need further investigation [9]. A recent paper has provided a new approach to shake-off calculations [10]. Large, relativistic, multiconfiguration calculations have been performed for the $3d$-transition metal series. These atomic models have been used in a multiconfiguration shake-off calculation and have provided new *ab initio* shake-off intensities which appear to be in better agreement with experiment than anything prior [9]. One of the first key observations within this framework is, of course, the treatment of correlation and, ergo, the derivation of the Moller or Breit interaction.

II. THE BREIT INTERACTION

In the MCDHF method, the atomic wave function becomes a linear combination of solutions to the central-field problem CSFs (symmetrized products of one-electron spinors) corresponding to different electron configurations,

$$\boldsymbol{\psi} = \sum_r c_r \boldsymbol{\psi}_r, \tag{1}$$

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where c_r is a set of mixing coefficients that are determined by diagonalizing the Dirac-Coulomb Hamiltonian ($q_i = q_j = -e$):

$$H = \sum_i \left(c\boldsymbol{\alpha_i} \cdot \boldsymbol{p_i} + q_i \phi(\boldsymbol{r_i}) + (\beta_i - 1) m_i c^2 + \sum_{i \geqslant j} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right). \tag{2}$$

The solutions of the self-consistent central-field Dirac equation form a complete, infinite basis set. As we let $r \to \infty$, the volume contains all significant amplitudes of the wave functions for all bound states of interest and so $\boldsymbol{\psi}$ should tend towards the exact solution of the Dirac equation. The Dirac-Coulomb Hamiltonian is the usual starting place for most relativistic atomic structure calculations. For example, the first-order relativistic corrections of this to the nonrelativistic Hamiltonian include the relativistic correction to the kinetic energy, the spin-orbit coupling, and the Darwin term.

Many authors have noted that the Dirac-Coulomb Hamiltonian, which includes only the instantaneous component of the Coulomb interaction, is both inconsistent with QED [11–13] and not covariant [14]. Breit [15,16] originally introduced additional terms to the Coulomb potential as a relativistic correction to the Gaunt interaction [17]. The original, classically derived "Breit interaction" (which includes the Gaunt interaction) is

$$B_{ij} = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} \left(\boldsymbol{\alpha_i} \cdot \boldsymbol{\alpha_j} - \frac{(\boldsymbol{\alpha_i} \cdot \boldsymbol{p_i})(\boldsymbol{\alpha_j} \cdot \boldsymbol{p_j})}{\hbar^2 m_i m_j} \right) \tag{3}$$

or

$$B_{ij} = \frac{e^2}{2\pi\epsilon_0} \left[\left(\frac{\boldsymbol{\alpha_i} \cdot \boldsymbol{\alpha_j}}{2r_{ij}} - \frac{(\boldsymbol{\alpha_i} \cdot \boldsymbol{r_{ij}})\boldsymbol{\alpha_j} \cdot \boldsymbol{r_{ij}}}{2r_{ij}^3} \right) - \frac{\boldsymbol{\alpha_i} \cdot \boldsymbol{\alpha_j}}{r_{ij}} \right] \tag{4}$$

in the Coulomb gauge. Equation 4 is usually interpreted as accounting for magnetic interactions between electrons (second term) and retardation of the electromagnetic interaction due to propagation at the speed of light (first term). As such, it includes orbit-orbit interactions (between the dipole moments of electrons or particles), spin-spin interactions (between the spins of electrons or particles), and spin-other-orbit interactions (between the spin of one electron or particle and the orbital angular momentum of another), as presented in many elementary atomic physics texts on the helium spectrum. Any complete relativistic formulation should be Lorentz covariant, so that the frame of reference can transform without the physical result being dependent upon the reference frame.

By treating the quantized electromagnetic field to lowest order in perturbation theory, the nonlocal generalization of the Breit interaction describing the exchange of a single transverse photon is

$$B_{ijC}(\omega) = -\frac{e^2}{4\pi\epsilon_0} \left\{ \boldsymbol{\alpha_i} \cdot \boldsymbol{\alpha_j} \frac{\cos(\omega r_{ij}/c)}{r_{ij}} - \left[\frac{(\boldsymbol{\alpha_i} \cdot \boldsymbol{p_i})}{\hbar m_i} \left(\frac{(\boldsymbol{\alpha_j} \cdot \boldsymbol{p_j})}{\hbar m_j} \frac{\cos(\omega r_{ij}/c) - 1}{\omega^2 r_{ij}/c^2} \right) \right] \right\}, \tag{5}$$

where ω is the angular frequency of the virtual photon [18]. In the low-frequency limit this reduces to the original Breit interaction, however, the matrix elements are different in the Coulomb or transverse gauge ($\nabla \mathbf{A}(\mathbf{r},\mathbf{t}) = \mathbf{0}$) and the Lorenz (sometimes Feynman) gauge ($\nabla \mathbf{A}(\mathbf{r},\mathbf{t}) + \frac{1}{\mathbf{c}^2} \frac{\partial \phi}{\partial \mathbf{t}} = \mathbf{0}$), where

$$B_{ijL}(\omega) = \frac{e^2}{4\pi\epsilon_0} \left(\frac{\cos(\omega r_{ij}/c) - 1}{r_{ij}} - \boldsymbol{\alpha_i} \cdot \boldsymbol{\alpha_j} \frac{\cos(\omega r_{ij}/c)}{r_{ij}} \right). \tag{6}$$

Hata and Grant [19] applied this to simple configurations in F and B isoelectronic sequences and found that the interaction regains gauge invariance if applied to wave functions that satisfy the Dirac equation in a *local* potential and, also, compared the convergence of the approach and the contribution of the frequency-dependent component of the transverse photon correction to the QED contributions. They found that the frequency-dependent correction can contribute up to 10% of that from the frequency-independent Breit contribution [20]. The Coulomb gauge reduces easily to the nonrelativistic limit, whereas other gauges introduce terms that are only corrected in higher orders of QED. Hence almost all SCF calculations use the Coulomb gauge. For correlation orbitals the frequency of the exchange photon cannot be approximated by the eigenvalues of the orbitals; for them Koopman's theorem does not hold because they are only Lagrange parameters required by normalization constraint. A recent text discusses approaches to the formalism in some detail (Secs. 6.4.2 and 10.11 [21]), including imaginary contributions (mainly by using the exponential form rather than the real component).

The Dirac-Coulomb-Breit Hamiltonian contains all effects up to order α^2. The Breit interaction is the largest contributor to the Hamiltonian that is not included in the self-consistent optimization process. Early authors believed that inclusion of the Breit interaction in self-consistent field calculations would prove extraordinarily difficult [22,23]. In the late 1950s, Bethe and Salpeter [22] argued that the Breit interaction should not be included self-consistently, as the Breit interaction is invalid in matrix form when negative energy states are included. Kim [23] had problems now known to be due to his choice of basis set; his spinor components were not kinetically matched, so that he experienced all the traditional pathologies, although his Z was low enough for them to appear puzzling but not fatal to the computation. Much later, a number of groups argued that it was possible for the Breit interaction to be included self-consistently [14,24] as imagined by Grant [25]. This has been shown to be true, and the matrix elements have been given in forms suitable for computation [14,26,27] for the frequency-independent contribution. Other authors have argued that the negative-energy states could be regularized using projection operators, but this led to very large computational challenges. Lindroth [28] argued that the previously observed problems with self-consistent inclusion of the Breit interaction were a *symptom* of "variational collapse" and not the cause of the problem.

Arguments have been applied that the frequency-dependent contribution is small, can be treated in perturbation, and must be treated in perturbation since it relates to virtual photons and virtual photon cancellation with QED Feynman diagrams in the same order, which will tend to be of

TABLE I. Convergence of the total and Breit energy contribution to the ground state of several noble gases and alkaline metals calculated using the perturbative approach described in the text. Results are compared to the self-consistent results of Ishikawa *et al.* [29] and Parpia *et al.* [30]. N_{csf} is the number of configuration state functions, E_{DC} is the Dirac-Coulomb energy, $E_{\mathrm{DC+B}}$ is the Dirac-Coulomb-Breit energy, and E_B is the Breit energy. The Breit contributions agree to within 5% and, in many cases, to approximately 1%. Values are given in atomic units, and the speed of light used in these calculations was 137.0370 a.u.

			N_{csf}	E_{DC}	$E_{\mathrm{DC+B}}$	E_B	Discrepancy
10	Ne	$2p$	1	128.69193051	128.67529063	0.01663988	
		$3p$	38	128.82217580	128.80559593	0.01657987	
		$4p$	130	128.86147359	128.84570363	0.01576995	
		$5p$	**277**	**128.87224391**	**128.85649251**	**0.01575140**	
		Ishikawa		**128.69177653**	**128.67513577**	**0.01664076**	**5.3%**
		Parpia		**128.69193**	**128.67529**	**0.01664364**	**5.4%**
12	Mg	$3s$	1	199.9350669	199.9032457	0.0318212	
		$3p$	27	199.9669607	199.9351365	0.0318241	
		$4p$	**138**	**200.0774388**	**200.0457316**	**0.0317071**	
		Ishikawa		**199.9347886**	**199.9029617**	**0.0318269**	**3.8%**
		Parpia		**199.93506**	**199.90323**	**0.0318336**	**4.0%**
18	Ar	$3p$	1	528.6837624	528.5515487	0.1322137	
		$4p$	103	528.7913500	528.6595800	0.1317699	
		$5p$	380	528.8371574	528.7054259	0.1317314	
		$6p$	**832**	**528.8750996**	**528.7460524**	**0.1290471**	
		Ishikawa		**528.6833606**	**528.5510378**	**0.1323228**	**2.5%**
		Parpia		**528.68379**	**528.55147**	**0.1323647**	**2.5%**
20	Ca	$4s$	1	679.710160	679.5193798	0.1907802	
		$4p$	63	679.737280	679.5464537	0.1908264	
		$5p$	**343**	**679.837809**	**679.6476017**	**0.1902079**	
		Ishikawa		**679.709594**	**679.5186001**	**0.1909940**	**0.4%**
		Parpia		**679.71022**	**679.51922**	**0.1910617**	**0.5%**
36	Kr	$4p$	1	2788.860581	2787.4410847	1.419496	
		$4f$	591	2789.257121	2787.839085	1.418036	
		$5f$	**3578**	**2789.719095**	**278.307393**	**1.411702**	
		Ishikawa		**2788.856297**	**2787.430523**	**1.425874**	**1.0%**
		Parpia		**2788.8622**	**2787.4362**	**1.426806**	**1.1%**
38	Sr	$5s$	1	3178.079907	3176.370006	1.709901	
		$5d$	1410	3178.495333	3176.787028	1.708305	
		$6d$	**4356**	**3178.754645**	**3177.056160**	**1.698485**	
		Ishikawa		**3178.074209**	**3176.355672**	**1.718537**	**1.2%**
54	Xe	$5p$	1	7446.894386	7441.183726	5.71066	
		$5d$	345	7446.981879	7441.267993	5.713885	
		$6d$	**3223**	**7447.357717**	**7441.655062**	**5.702654**	
		Ishikawa		**7446.894950**	**7441.125194**	**5.769756**	**1.2%**
		Parpia		**7446.9032**	**7441.1333**	**5.775339**	**1.3%**

greater magnitude. In the Breit (long-photon-wavelength) approximation—it is useful to make the distinction between Breit's interaction and the full transverse photon interaction—the interelectronic potential does not depend on the orbital eigenvalues, so that the self-consistent calculation is similar in scope to that using only the Coulomb potential. If the electron-electron interaction depends on the frequency (eigenvalue difference) of the exchanged virtual photon, one has a very complicated iterative problem and no idea if there is a true mathematical solution of the coupled SCF equations. Moreover, it does not sit very well within the usual Furry picture, which assumes that there is a well-defined complete set of orbital spinors which forms the scaffold on which everything hangs. SCF calculations define the effective one-body potential generating the space spanned by these spinors.

Several atomic structure packages have included the frequency-independent Breit interaction in the Coulomb gauge at the radial optimization stage [28–32]. Interestingly, the popular and successful RCCC method implemented a Breit component only in 2009, using the Feynman or Lorenz gauge and hence the Moller interaction [33]. Interestingly, this Moller implementation appears to include the full frequency-dependent transverse photon operator [34]. Inclusion of the Breit interaction has been implemented in the GRASP packages at the configuration-interaction (perturbation) level. Further discussion of the detailed background is given in [21] and [35].

III. CONVERGENCE OF BREIT INTERACTION ENERGIES

In the work presented here we include the Breit interaction at the configuration-interaction level. In other words, we optimize the radial wave functions without considering the effect of Eq. (5), but following optimization we compute the eigenfunctions of the full Hamiltonian including the Breit interaction and QED effects. In the limit that the CSF basis approaches completeness these two methods are equivalent. In the present section, we wish to consider how the perturbative inclusion of the Breit interaction in the GRASP2K package compares to (such) self-consistent implementations.

Ishikawa *et al.* [29,31] performed relativistic self-consistent calculations with the Breit interaction using Gaussian basis sets. They investigated a number of Be-like and Ne-like atoms. Parpia *et al.* [30] also look at the Breit interaction self-consistently, using Gaussian basis sets and including finite nuclei. Their results agree quite closely with those of Ishikawa. In Table I we compare the Breit interaction as calculated in GRASP2K with the results of Ishikawa.

When correlation orbitals are not included in the calculation, it is clear that the Breit interaction calculated using GRASP2K is highly discrepant. As we increase the number of correlation orbitals, however, the energy contribution of the Breit interaction quickly converges to the values in [31]. The maximum fractional discrepancies occur in systems where the Breit contribution is small—in neon our value differs from Ishikawa by 5%. The maximum absolute discrepancies occur in strontium and krypton, where the discrepancy is ≈0.5 eV, however, in both cases uncertainty in the energy convergence is greater, and it is probable that a larger basis set will improve these values. In other words, this discrepancy is not the factor limiting accuracy, and the dominant contribution to uncertainty and systematic error is the completeness and convergence of the wave function and not the form of the implementation of the Breit operator.

IV. CONVERGENCE OF BREIT INTERACTION MIXING COEFFICIENTS

Indelicato *et al.* [32] point out that the inclusion of the Breit interaction during radial optimization not only affects energies, but also affects mixing coefficients. This can be vital for weak or forbidden transition rates and other values not related to energy. Indelicato *et al.* compare the mixing coefficients of the $1s2p\,^3P_1$ state in the $J-J$ coupled basis calculated using no Breit interaction and using a self-consistent Breit interaction. In the $J-J$ representation, the $1s2p^3P_1$ state can be written

$$|1s2p\,^3P_1\rangle = c_1|1s2p_{1/2}J=1\rangle + c_2|1s2p_{3/2}J=1\rangle, \quad (7)$$

with the ratio c_1:c_2 being strongly influenced by the Breit interaction at high Z.

Indelicato *et al.* test this using two methods of calculation. In the first the Breit interaction is not included, and in the second it is included self-consistently. We have reproduced Indelicato *et al.*'s results in which the Breit interaction is excluded and have extended this by also considering the inclusion of the Breit interaction as a perturbation. The results are presented in Fig. 1. Our results for the mixing coefficients calculated using only the Coulomb interaction (omitting the Breit interaction) are nearly identical to those of Indelicato *et al.* The mixing coefficients that we have determined using

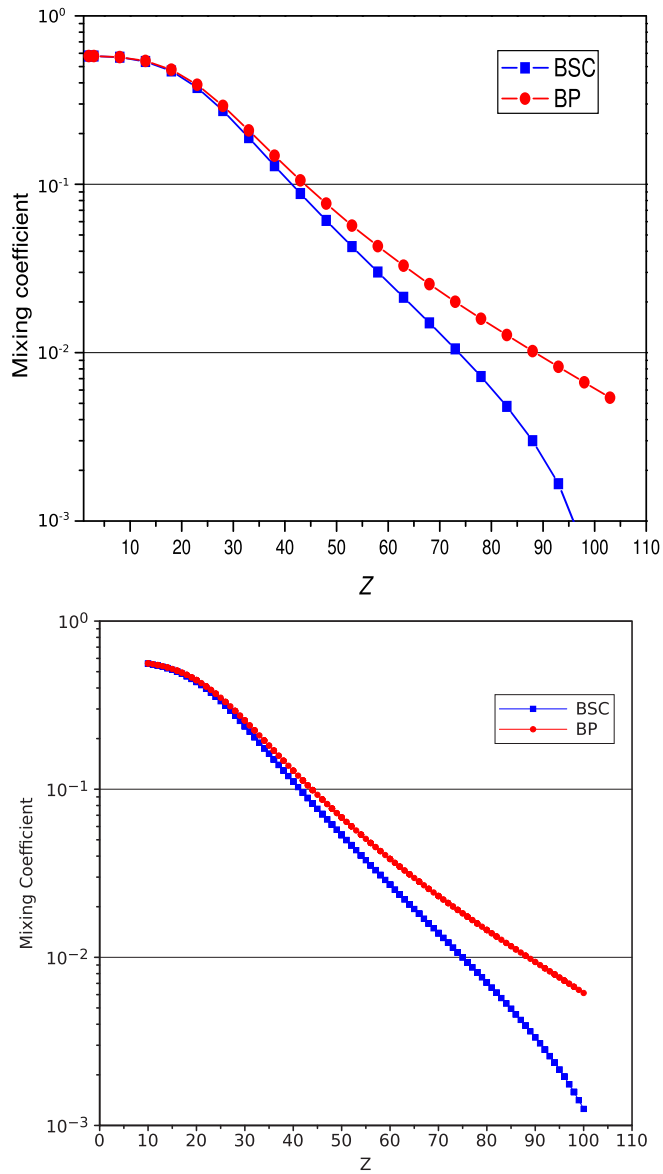

FIG. 1. (Color online) Comparison of the c_2 mixing coefficient for the $1s2p\,^3P_1$ level of helium-like ions calculated with self-consistent [32] and perturbative inclusion of the Breit interaction (present work). Values calculated using only the Coulomb interaction are very similar to those of Indelicato *et al.*, suggesting an accurate reproduction of their wave functions. The c_2 mixing coefficient differs slightly using a perturbative Breit interaction compared to the self-consistent calculation of Indelicato *et al.*, which could have implications for the calculation of highly sensitive weak or forbidden transition rates. Top: Reproduced from Indelicato *et al.* [32]: Variation with Z of the mixing c_2 coefficient for the $1s2\,^3P_1$ level of helium-like ions. BP: only the Coulomb interaction is used in the SCF process. BSC: the full Breit interaction is used in the SCF process. Bottom: Variation with Z of the mixing c_2 coefficient, from the present work. BP: only the Coulomb interaction is used in the SCF process. BSC: the Breit interaction is added perturbatively after wave-function optimization.

a perturbative Breit interaction differ only very slightly from those calculated by Indelicato *et al.* self-consistently.

Figure 1 provides no support for the conclusion of Indelicato *et al.* that the mixing coefficients can be significantly altered due to the Breit interaction's effect on wave functions when included during radial optimization. Since the wave functions used in our work use a different basis from those used by Indelicato *et al.*, we *expect* there to be small differences in the mixing coefficients, but these appear negligible. In order to determine whether these possible differences have any impact on predictions of physical values—or are just a manifestation of using a slightly different basis set—we need to investigate further.

In principle, past work can be updated to include the additional interaction in perturbation or to just compute the relevant Breit interaction. However, we note that such a correction will mainly work if (and only if) the original CSF array is the same as in the recalculation; otherwise, the correlated correction will be different, as seen in the current example. A full recomputation to convergence is often needed.

V. CONVERGENCE OF BREIT INTERACTION (RELATIVISTIC) TRANSITION PROBABILITIES

In order to test the influence of the Breit interaction on transition rates, we consider next the $K\alpha$ hypersatellites (arising from the $1s^{-2} \rightarrow 1s^{-1}2p^{-1}$ transition). The Breit interaction is of significant importance in the calculation of the $K\alpha$ hypersatellites: partial cancellation of the Coulomb interaction results in the Breit interaction's contributing more significantly than in most transitions [36,37]. The transitions are also strongly influenced by QED effects, and the intensity ratio is influenced by both relativistic contributions and the Breit term.

Consequently, the transitions have been the focus of many theoretical and experimental investigations. Their sensitivity to the Breit interaction makes them a useful test for the perturbative implementation. The ratio is especially useful for testing whether the perturbative inclusion of the Breit interaction has any effect on transition rates, as the Breit interaction contributes up to 70% of the transition ratio.

In Fig. 2 we compare our calculations of the $K\alpha_1^h/K\alpha_2^h$ intensity ratio to the theoretical and experimental results of other authors. Our results are in good agreement with both the theoretical and the experimental results. This agreement, in a system highly sensitive to the Breit effect, evinces that perturbative inclusion of the Breit interaction is sufficient for accurate determination of transition rates in this system.

Costa *et al.* [38] have recently carried out a determination of the $K\alpha^h$ intensity ratio using a self-consistent implementation of the Breit interaction. The Breit interaction alters the intensity ratio by up to 70%, and we have plotted the relative contribution of the Breit interaction calculated using our own implementation and as reported by Costa *et al.* (Fig. 3). Despite the large contribution from the Breit interaction and the differences in the two methods, the results are in excellent agreement. The maximum discrepancy occurs at $Z = 12$, where the contribution of the Breit interaction differs by ~2.5

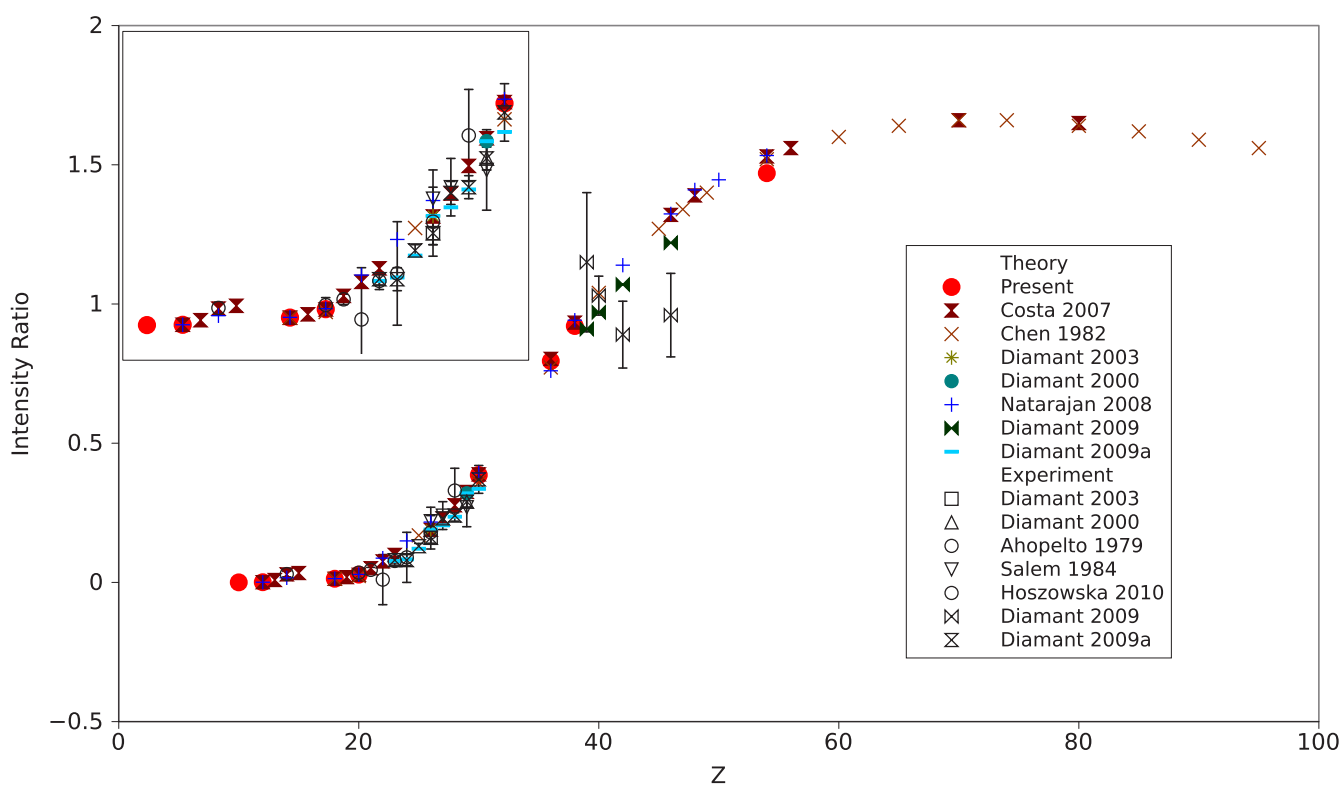

FIG. 2. (Color online) The $K\alpha_1^h/K\alpha_2^h$ intensity ratio as calculated in the present work, compared to theoretical predictions using both self-consistent and perturbative Breit interactions and experiment. The $K\alpha^h$ intensity ratio is highly sensitive to contributions from the Breit interaction. Our results, using a perturbative approach, are consistent with all experimental values and are in good agreement with all other theoretical values.

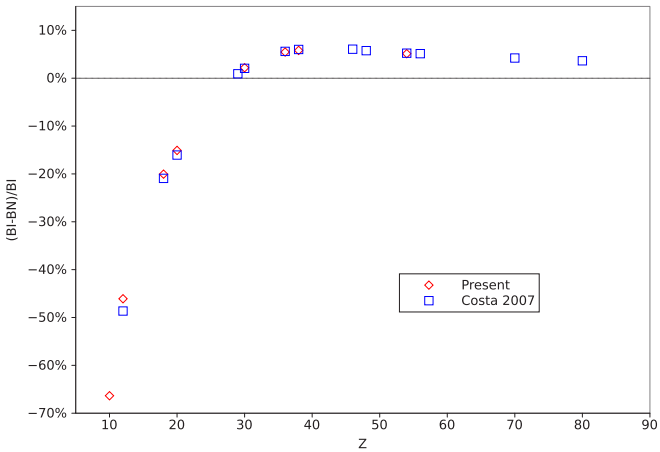

FIG. 3. (Color online) Effect of the Breit interaction on the $K\alpha_1^h/K\alpha_2^h$ ratio. The present results, calculated using a perturbative Breit interaction, are compared to the recent results of Costa *et al.* [38], who used a self-consistent implementation of the Breit interaction. Although the ratio is significantly affected by the Breit interaction, the results of the two methods are practically identical.

percentage points (Fig. 4). In all other cases we obtain nearly identical contributions from the Breit term.

The results of this section have shown that, in most cases, calculating the Breit interaction using a self-consistent approach yields only a small difference from the configuration-interaction approach, and indeed there is a high likelihood that these small differences are due to the completeness and convergence of the wave functions and hence not to the form of implementation of the perturbative terms. In a beautiful study, Derevianko *et al.* [39] point out that gauge invariance requires the inclusion of negative-energy sates, at least with their basis set for transition probabilities for helium-like magnetic transitions. That study also discussed how some frameworks (basis sets) led to the negative-energy contribution vanishing. Earlier work discussed using projection operators to bypass difficulties with such an approach. Of course, ideal convergence also requires an infinite basis and an infinite set

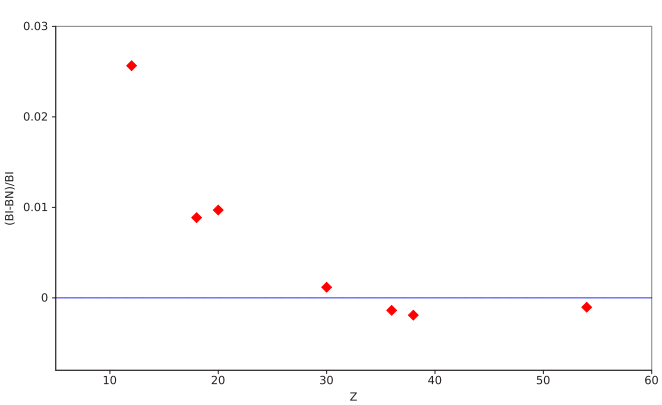

FIG. 4. (Color online) Discrepancy between the present calculation of the Breit interaction contribution to the $K\alpha_1^h/K\alpha_2^h$ ratio and the self-consistent calculation by Costa *et al.* [38]. The discrepancy is never large (2.5% at $Z = 12$), however, the agreement is better at higher atomic numbers.

of continuum states, but these are not usually required for any state-of-the-art convergence of gauge forms.

Although the mixing coefficients determined by Indelicato *et al.* [32] using a self-consistent approach differ slightly from our perturbative approach, we have found that neither eigenstate energies nor transition rates are affected by this difference. The error introduced by the Breit interaction approximations are much smaller than other sources of error such as convergence of transition energies with basis set expansion, even in the $K\alpha^h$ transitions, where the Breit interaction is the dominant contributor.

We note that in most cases we have demonstrated that any higher order terms (e.g., from the SCF approach) are quite small, especially compared to current convergence and computational limitations. Of course, these real additional terms including the frequency-dependent term are nonzero and should be observable in particular studies.

VI. CONVERGENCE OF THE BREIT INTERACTION IN X-RAY $K\alpha$, FORBIDDEN, AND UV-VIS TRANSITIONS

It has often been said that the relativistic many-body equations must be Lorentz covariant and that this requires computation of the frequency-dependent contributions to the full transverse photon operator rather than the low-frequency limit Breit operator. With no packages having investigated this in a detailed manner, we must currently abstain from appropriate conclusions, especially as the self-consistent implementation of QED terms often represents larger contributions to the energies.

It is well known that operators of relativistic Hamiltonians should be Lorentz covariant and, hence, that gauge transformations of operator forms must be completed between gauges, as evinced by Eqs. (5) and (6). However, claims have been made that the gauge convergence of *length (Babushkin) and velocity (Coulomb) forms of the relativistic (electric multipole) transition matrix operators* is (also) impossible without transformation of the operator form of the Breit interaction [40]. It should be remembered that the Coulomb or Lorenz (Feynman) gauge requires this transformation for convergence and that these choices are quite independent of the transition operator form. The convergence and accuracy of any computation between the length and the velocity forms depend upon the completeness of the wave function rather than the Breit operator form.

A similar claim relates to the difficulty of convergence of the characteristic x-ray spectra including complex satellites, such as for copper $K\alpha$ or titanium $K\alpha$; and to VUV forbidden transitions at low energies. A third claim relates to electric dipole (i.e., allowed) transitions of oxygen at low energies.

We find in recent studies [5,6,10,41] that the convergence of the length and velocity gauge forms is consistent and appears to find excellent agreement with experiment to a remarkable level, apparently unobstructed by the form of the Breit implementation. Similarly, we find, for the forbidden $E2$ and $M1$ 557.7- and 297.2-nm emission lines in oxygen [42], that dramatic improvements in convergence are possible and to an apparently arbitrary level subject to the completeness of the wave function. While it is inevitable that the form of the terms in the Hamiltonian and the methodology for

implementation must limit the final accuracy, we do not yet see these limitations. A separate methodical investigation of oxygen I and oxygen III electric dipole transition probabilities in different gauges also revealed the potential for dramatically improved gauge convergence, with no limitation yet from the perturbative versus self-consistent approaches [43]. In fact, for a set of these transitions we find reliable convergence to 0.02% in energies. We find that the forbidden (higher multipole) transitions are necessarily more strongly affected by the differences of the gauge form (Babushkin or Coulomb) than electric dipole operators and that, indeed, this is also likely to be due to the completeness of convergence of the relativistic wave functions over the active grid range.

VII. DISCUSSION

It remains true that development of relativistic atomic and molecular packages must increasingly investigate significant relativistic and higher order effects, especially including QED contributions [44], and in light of this, we particularly refer to Drake's accurate work on helium-like systems [35,45]. In part, they comment that the Breit-Pauli operators are dominant, followed by the lowest order QED Lamb shift self-energy, anomalous magnetic moment, and vacuum polarization terms, reduced mass corrections, and Wichmann-Kroll and higher-order Breit terms. Hence it is increasingly important to have reliable implementation of self-energy terms to compare many-electron atomic predictions of transition energies and amplitudes to a higher level of accuracy.

The electron-electron interaction in QED takes a different form depending on the gauge. Physical quantities should be gauge independent, but the fact that practical calculation involves approximation means that this is often far from achievable. Nonrelativistic calculations are a good starting point; here the Coulomb interaction dominates. In relativistic calculations this suggests adopting the Coulomb gauge, where the Coulomb interaction is supplemented by relativistic corrections (i.e., those vanishing in the nonrelativistic limit), which are usually treated as a perturbation to the DC Hamiltonian. The Breit interaction ($\omega = 0$) can, in principle, either be treated simply as a perturbation or be incorporated in SCFs. The DCB SCF is computationally time-consuming and difficult to program in GRASP-style calculations using integrodifferential equations. It is much more straightforward to do the calculation using matrix methods. We identify transitions which are sensitive to the Breit interaction. Some calculations have been done using DCB, but it is not clear that it is necessary to treat the construction of trial wave functions in this way; the effect of self–consistency on wave functions is small in all cases treated so far. This investigation supports the idea that most problems can be treated satisfactorily using DC + B wave functions.

The effect of using the Breit operator in configuration interactions compared to a self-consistent implementation is, at most, equivalent to a higher order correction of perturbation theory. Currently we are able to compute (with challenges) transition rates to better than 1% accuracy, and transition rates to 2.5% in extreme cases where the rate is fully dominated by the Breit interaction. Energies are generally more stable for electric dipole allowed transitions, and, e.g., ground-state energies are usually able to be obtained with accuracies approaching or exceeding 1% and, in a number of cases, possibly 0.02%. Complex characteristic energies of x-ray spectra can now approach accuracies approaching 0.001%, 0.1 eV, or 10 ppm; and transition probabilities, accuracies of 0.01%–0.03%. In general these levels of convergence can only become accuracies with the inclusion of first-order Breit and QED terms including self-energy terms, which can have magnitudes in relevant transitions of 10–100 ppm or more. The full transverse photon interaction can contribute up to 10% of the frequency-independent Breit form. Self-consistent higher order perturbative corrections may contribute at or below this level. Stark and Zeeman effects can easily dominate over these perturbations in relevant experiments, as can the hyperfine structure.

At the current level of potential convergence, which surely depends upon the quantum system of interest, it is most commonly the extension in a stable manner to a converged and complete wave function which remains the driving force towards a higher accuracy. For one-electron and two-electron systems, explicit and high-level computations of QED enable significantly higher accuracies than these current levels but remain an additional challenge.

The Breit interaction is the largest contributor to the atomic Hamiltonian that is sometimes not included self-consistently. Several other implementations of the MCDHF method have implemented the Breit interaction self-consistently. We have tested our implementation of the Breit interaction and found that it produces energy results that are in excellent agreement with self-consistent implementations. In the limit that the number of CSFs tends to infinity our results will be virtually identical to the results obtained through a self-consistent Breit implementation, although the specific basis states and mixing coefficients will differ.

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