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Breit corrections to individual atomic and molecular orbital energies

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Several issues concerning Breit correction to electron-electron interaction in many-electron systems, which are important in precise atomic and molecular calculations, are presented. At first, perturbative versus self-consistent calculations of Breit correction were studied in selected cases. Second, the Z-dependence of Breit contribution per subshell is shown, based on values calculated for selected atoms with $30 \leq Z \leq 118$. Third, the relations between magnetic and retardation parts of Breit interaction are analyzed. Finally, Gaunt contribution calculated for Kr, Xe, and Rn noble gas atoms and its isoelectronic HBr, HI, and HAt diatomic molecules has been compared to full-Breit atomic calculations. We found that Breit corrections should be treated by self-consistent calculations and that there is a functional dependence of those corrections for subshells as $\varepsilon_{nl}^{Breit}(Z) \simeq a \times Z^b$. We also found that molecular Gaunt corrections are close to their atomic counterparts for inner electrons though they are not for outer orbitals. In any case, accurate calculations must include retardation correction in addition to Gaunt. *Published by AIP Publishing.* https://doi.org/10.1063/1.5017986

I. INTRODUCTION

Calculations of both atomic structure and properties for the medium to high atomic number range require careful consideration of relativistic effects.[1] The Breit interaction gives the leading relativistic correction to the instantaneous Coulomb electron–electron interaction potential in quantum electrodynamics. Its inclusion is required for precision calculations of binding energies and transition rates in heavy atoms.[2]

There has been an intensive discussion in the past years on whether the two-electron Breit interaction terms should be used perturbatively or variationally.[3–7] Breit[8–10] and later Bethe and Salpeter[3] pointed out that the Breit operator should only be treated as a first-order perturbation because its inclusion in an unperturbed Hamiltonian would led to a result inconsistent with quantum electrodynamics. On the other hand, more recently Quiney *et al.*[6] and Ishikawa *et al.*[11,12] have shown that the correct inclusion of the Breit term in the self-consistent-field procedure does not lead to "variational collapse"[13] or to a result inconsistent with quantum electrodynamics. In line with this, Grant *et al.*[14,15] pointed out that a variational procedure for Breit terms is preferred in a subsequent treatment of electron correlation. Moreover, Lindroth *et al.*[16] stated that a variational self-consistent treatment of the Breit interaction is very important for properties of orbitals, especially for the valence ones, in many-electron systems.

On the other hand, Chen *et al.*[17] and further Costa *et al.*[18] reported that the $K^h\alpha_1/K^h\alpha_2$ line intensity ratio is sensitive to the inclusion of the Breit interaction. They found that for low-Z elements the inclusion of the Breit term decreases the $K^h\alpha_1/K^h\alpha_2$ ratio by 48% (Z = 12) to 20% (Z = 20). For medium- and high-Z atoms ($Z \gtrsim 30$), the effect is reversed, meaning that including the Breit term increases the $K^h\alpha_1/K^h\alpha_2$ ratio by about 5%-7%. Pernpointner[19,20] showed that Breit-type integrals at the SCF level exhibit a weak but noticeable effect for molecular properties, such as electric field gradient and ionization spectrum, of TlH. Further studies of Quiney *et al.*[21] focused on the effect of Breit corrections to the potential energy surface and vibration–rotation levels of water. Beside, Thierfelder and Schwerdtfeger pointed out[22] that the variational treatment of the Breit interaction achieves Koopmans theorem.

Recently, Chantler *et al.*[23] studied the convergence of the Breit interaction in self-consistent and configuration-interaction approaches. The Z-dependence of Breit contribution to the total energy of the ground state of selected atoms with $2 \leq Z \leq 102$ has been studied by Mann and Johnson,[24] and $Z^{3.6}$ dependence has been found. They also studied the relative importance of magnetic (Gaunt) and retardation parts of the Breit interaction and found that the energy shift due to retardation is about 10% of the Gaunt energy shift for ground states of atoms in the range $Z = 2$–$Z = 102$, and that the Gaunt and the retardation contributions are of opposite signs. In the extensive study of Huang *et al.*,[25] the Breit contributions to the orbital binding energies for all atoms with $2 \leq Z \leq 106$ have been presented. Niskanen *et al.*[26] found that the Gaunt contribution to the single and double 1s electron ionization energies of noble gases scales approximately as $Z^{3.3}$.

Including the Breit interaction term in the self-consistent-field procedure using the Gaussian basis set, applying to general-purpose molecular calculations, was established well last years.[29–31] However these studies implement only the dominant magnetic part of the Breit interaction in calculations.

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In this work, we show new insights about several issues concerning Breit correction, which are important in precise atomic and molecular calculations. At first, results of perturbative and self-consistent calculations of Breit correction are analyzed in selected atomic systems. Second, the Z-dependence of Breit contribution per subshell is shown, based on values calculated for selected atoms with $30 \leq Z \leq 118$. Third, the relations between magnetic and retardation parts of Breit interaction have been studied. Finally, Gaunt contributions calculated for Kr, Xe, and Rn noble gas atoms and its iso-electronic HBr, HI, and HAt diatomic molecules are compared with full-Breit atomic calculations. We want to give new insights on the behavior of Breit and Gaunt corrections to the atomic or molecular orbital energies of atoms and diatomic molecules.

II. THEORETICAL BACKGROUND

A. MCDF methods

The methodology of Multi-Configuration Dirac-Hartree-Fock (MCDF) calculations performed in the present studies is similar to the one published earlier, in several papers (see, e.g., Refs. 32–37). The effective Hamiltonian for an N-electron system is expressed by

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_D(i) + \sum_{j>i=1}^{N} V_{ij}, \tag{1}$$

where $\hat{h}_D(i)$ is the Dirac one-particle operator for the ith electron and the terms $\hat{V}_{ij}$ account for the effective electron-electron interactions and depend on the photon propagator. When considering the virtual one-photon exchange, it may be expressed in any of the two gauges, the Feynman (Lorentz) gauge or the Coulomb gauge. They do have different actual expressions that need to be clarified because they will be used in this work.[38]

The interaction potential in the Feynman gauge (also called the Møller interaction[39]) is

$$\hat{V}_{ij(F)} = \left(1 - \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j\right) \frac{e^{i\omega_{ij} r_{ij}}}{r_{ij}}, \tag{2}$$

and in the Coulomb gauge it is

$$\hat{V}_{ij(C)} = \left[\frac{1}{r_{ij}} - \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j \frac{e^{i\omega_{ij} r_{ij}}}{r_{ij}} - (\boldsymbol{\alpha}_i \cdot \boldsymbol{\nabla}_i)(\boldsymbol{\alpha}_j \cdot \boldsymbol{\nabla}_j) \frac{e^{i\omega_{ij} r_{ij}} - 1}{\omega_{ij}^2 r_{ij}}\right]. \tag{3}$$

The latter is a sum of the Coulomb interaction $\hat{V}_{ij}^C$ operator and the transverse Breit $\hat{V}_{ij}^B$ operator,[8–10]

$$\hat{V}_{ij} = \hat{V}_{ij}^C + \hat{V}_{ij}^B, \tag{4}$$

where the Coulomb interaction operator is $\hat{V}_{ij}^C = 1/r_{ij}$, and $\omega_{ij} = (\varepsilon_i - \varepsilon_j)/c$ is the frequency of the one virtual photon exchanged[39] (ε_i and ε_j are the orbital energies of interacting electrons).

The unretarded (instantaneous) parts are obtained by applying the long wavelength approximation: $\omega_{ij} \to 0$. Then within the Feynman gauge, the Coulomb-Gaunt interaction terms are

TABLE I. Energy contribution per subshell of Breit interaction for $_{80}$Hg (eV units), calculated with perturbational (PT) and self-consistent (SC) approaches. PT means the frequency-dependent Breit operator and PT* means the frequency-independent Breit operator [Eq. (7)].

	Present			Reference 16		Reference 22		Reference 24	Reference 27
	PT	PT*	SC	PT*	SC	PT*	SC	PT	SC
$1s$	309.497	315.893	298.329	315.11	298.24	312.191	298.661	308.147	298.329
$2s$	42.129	41.823	33.456	41.72	33.47	41.981	33.486	42.13	33.456
$3s$	9.729	9.653	6.191	9.636	6.193	9.926	6.198	9.729	6.191
$4s$	2.519	2.5	1.269	2.496	1.270	2.761	1.272	2.52	1.269
$5s$	0.498	0.494	0.191	0.493	0.191	0.568	0.192	0.498	0.191
$6s$	0.042	0.042	0.012	0.042	0.012	0.038	0.012	0.042	0.012
$2p_{1/2}$	65.502	65.663	56.253	65.47	56.25	66.549	56.259	65.499	56.253
$3p_{1/2}$	14.47	14.375	10.703	14.338	10.702	15.397	10.704	14.47	10.703
$4p_{1/2}$	3.529	3.5	2.269	3.491	2.269	4.153	2.269	3.528	2.269
$5p_{1/2}$	0.6	0.595	0.33	0.593	0.330	0.778	0.33	0.6	0.33
$2p_{3/2}$	41.149	44.024	35.507	43.92	35.51	45.457	35.505	41.146	35.507
$3p_{3/2}$	9.156	9.756	6.386	9.736	6.387	11.147	6.386	9.155	6.386
$4p_{3/2}$	2.185	2.327	1.186	2.322	1.186	3.203	1.186	2.184	1.186
$5p_{3/2}$	0.351	0.374	0.131	0.373	0.131	0.628	0.131	0.351	0.131
$3d_{3/2}$	8.32	8.322	4.648	8.305	4.648	9.369	4.648	8.32	4.648
$4d_{3/2}$	1.749	1.747	0.625	1.743	0.625	2.405	0.625	1.75	0.625
$5d_{3/2}$	0.166	0.165	0.007	0.165	0.007	0.273	0.007	0.166	0.007
$3d_{5/2}$	6.501	6.56	2.99	6.547	2.988	7.619	2.989	6.501	2.99
$4d_{5/2}$	1.341	1.352	0.26	1.350	0.260	1.972	0.26	1.342	0.26
$5d_{5/2}$	0.119	0.12	−0.03	0.120	−0.030	0.219	−0.03	0.118	−0.03
$4f_{5/2}$	0.762	0.747	−0.158	0.760	−0.158	1.218	−0.158	0.762	−0.158
$4f_{7/2}$	0.598	0.588	−0.312	0.597	−0.313	1.032	−0.313	0.597	−0.312

$$\hat{V}_{ij(F)}(\omega_{ij}=0)=\frac{1}{r_{ij}}(1-\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j)=\hat{V}^C_{ij}+\hat{V}^G_{ij}, \tag{5}$$

where $-(\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j)/r_{ij}$ is called the Gaunt (magnetic) term.[40] Within the Coulomb gauge, the Coulomb-Breit terms are given as

$$\hat{V}_{ij(C)}(\omega_{ij}=0)=\frac{1}{r_{ij}}\left(1-\frac{1}{2}\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j-\frac{(\boldsymbol{\alpha}_i\cdot r_{ij})(\boldsymbol{\alpha}_j\cdot r_{ij})}{2r^3_{ij}}\right). \tag{6}$$

In the above equation, the Breit $\hat{V}^B_{ij}$ operator is written in the zero-frequency limit ($\omega_{ij}\to 0$) as

$$\begin{aligned}\hat{V}^B_{ij}&=-\frac{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j}{2r_{ij}}-\frac{(\boldsymbol{\alpha}_i\cdot r_{ij})(\boldsymbol{\alpha}_j\cdot r_{ij})}{2r^3_{ij}}\\&=\underbrace{-\frac{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j}{r_{ij}}}_{V_G}+\underbrace{\left(\frac{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j}{2r_{ij}}-\frac{(\boldsymbol{\alpha}_i\cdot r_{ij})(\boldsymbol{\alpha}_j\cdot r_{ij})}{2r^3_{ij}}\right)}_{V_{ret}},\end{aligned} \tag{7}$$

where V_{ret} is called the gauge term or, commonly but somewhat misleadingly, retardation part. In this equation, the frequency-dependent term of order $O(\omega^2)$ is omitted.

Gorceix *et al.*[36] and Gorceix and Indelicato[46] have found that the interaction potentials derived in the Coulomb and Feynman gauges, respectively, lead to significantly different numerical results in a MCDF calculation. Sucher[47] found that, in contrast to the Coulomb gauge, the non-perturbative use of potential in the Feynman gauge leads to energy levels which are already incorrect in order $\alpha^4 m$, even if the frequency dependence is included. Lindroth and Mårtensson-Pendrill[48] have examined the gauge dependence further and found that the discrepancy remains, even if one goes beyond the no-virtual-pair approximation. This fact provides a quantitative argument for preferring the Coulomb gauge over the Feynman gauge. Lindgren[49] demonstrated that within the no-virtual-pair approximation both the gauges yield the same energy shift to order $O(\alpha^2$ hartree) only if the irreducible part of the two-photon interaction in the Feynman gauge is also taken into account.

The zero-frequency approximation to the full transverse Breit interaction, i.e., Eq. (7), is more common in computations of many-electron atomic systems than the explicit frequency-dependent form because of remedying the lack of covariance of the Dirac-Coulomb-Breit Hamiltonian. The differences of state energy calculated by using frequency-independent and frequency-dependent Breit operators are found to be small.[16,36,50] For the super-heavy Rn-like ions with $Z = 170$, Indelicato[51] found that the frequency-dependent term contribute −1.3% (having opposite sign) of the total Breit correction to $1s$ binding energy. The finite ω corrections were studied in the work of Beatham *et al.*[52] in the case of $K\alpha_{1,2}$

TABLE II. Energy contribution per subshell of Breit interaction for $_{30}$Zn, $_{54}$Xe, and $_{102}$No, calculated with perturbational (PT) and self-consistent (SC) approaches. PT means the frequency-dependent Breit operator and PT* means the frequency-independent Breit operator [Eq. (7)].

	Zn			Xe				No				
							Reference 12				Reference 27	Reference 28
	PT	PT*	SC	PT	PT*	SC	SC	PT	PT*	SC	SC	SC
$1s$	13.135	13.171	11.875	86.036	86.883	80.712	80.709	718.755	739.879	703.058	703.145	703.142
$2s$	1.324	1.322	0.851	10.432	10.392	7.634	7.633	107.558	106.498	88.649	88.669	88.682
$3s$	0.195	0.195	0.090	2.110	2.101	1.101	1.101	26.547	26.297	18.434	18.437	18.436
$4s$	0.008	0.008	0.003	0.447	0.445	0.153	0.153	7.795	7.720	4.561	4.562	4.562
$5s$				0.019	0.058	0.008	0.007	2.270	2.248	1.140	1.140	1.140
$6s$								0.700	0.693	0.213	0.213	0.213
$7s$								0.255	0.252	0.007	0.007	0.007
$2p_{1/2}$	2.018	2.020	1.503	16.066	16.106	13.045	13.045	169.722	169.395	149.061	149.064	149.064
$3p_{1/2}$	0.257	0.255	0.160	3.072	3.069	2.034	2.034	39.810	39.138	30.699	30.700	30.700
$4p_{1/2}$				0.591	0.590	0.314	0.315	11.133	10.919	7.654	7.655	7.655
$5p_{1/2}$				0.014	0.057	0.020	0.020	3.047	2.986	1.852	1.852	1.853
$6p_{1/2}$								0.897	0.879	0.295	0.295	0.296
$2p_{3/2}$	1.486	1.502	0.976	11.407	11.781	8.815	8.814	88.814	98.656	81.813	81.812	81.814
$3p_{3/2}$	0.187	0.188	0.085	2.168	2.236	1.228	1.228	21.339	23.544	16.336	16.336	16.335
$4p_{3/2}$				0.413	0.426	0.151	0.151	5.832	6.437	3.629	3.629	3.629
$5p_{3/2}$				0.076	0.039	0.003	0.003	1.573	1.737	0.764	0.764	0.764
$6p_{3/2}$								0.460	0.508	0.083	0.083	0.083
$3d_{3/2}$	0.086	0.084	0.005	1.704	1.704	0.630	0.630	20.982	21.036	13.268	13.268	13.268
$4d_{3/2}$				0.245	0.243	0.006	0.006	5.306	5.306	2.459	2.459	2.459
$5d_{3/2}$								1.260	1.259	0.378	0.378	0.378
$3d_{5/2}$	0.064	0.062	−0.022	1.337	1.342	0.277	0.277	16.115	16.365	8.979	8.979	8.980
$4d_{5/2}$				0.187	0.187	−0.052	−0.052	4.025	4.080	1.381	1.381	1.381
$5d_{5/2}$								0.946	0.959	0.133	0.133	0.134
$4f_{5/2}$								2.866	2.862	0.293	0.293	0.293
$5f_{5/2}$								0.001	0.001	−0.088	−0.088	−0.088
$4f_{7/2}$								2.284	2.290	−0.217	−0.218	−0.217
$5f_{7/2}$								0.002	0.002	−0.156	−0.156	−0.156

TABLE III. 1*s* ionization potential for Xe (eV).

	Xe (neutral)	Xe (1s hole)	IP (1s)
DC	−202 639.438	−167 952.784	34 686.654
+Breit (SC)	155.104	73.597	−81.506
mag.	174.930	86.169	−88.761
ret.	−18.073	−11.595	6.478
ω-dep.	−1.753	−0.976	0.776
+Breit (PT)	155.395	73.687	−81.708
mag.	175.261	86.278	−88.983
ret.	−18.107	−11.613	6.494
ω-dep.	−1.759	−0.978	0.781
+SE	118.650	70.558	−48.092
+VP	−16.520	−9.575	6.946
Total (SC)	−202 382.205	−167 818.203	34 564.001
Total (PT)	−202 381.636	−167 818.065	−34 563.571
Theory			
Indelicato *et al.*[41]			34 566.52
Deslattes *et al.*[42]			34 566.5(26)
Niskanen *et al.*[26]			34 598.0
Barysz and Syrocki[43]			34 532.59
Experiment			
Bearden and Burr[44]			34 561.4(11)
Deutsch *et al.*[45]			34 563.4
Deslattes *et al.*[42]			34 565.13(33)

and $K^h\alpha_{1,2}$ lines of Hg. They found that the finite ω corrections contribute −2.4% and −1.8% to the total Breit energy contribution in the case of single 1*s*- and 2*p*-shell ionized Hg atoms, respectively.

The Breit interaction can be included in two general ways: in the self-consistent field process, such as in the MCDFGME code,[36,53–55] or in the perturbational approach, such as in the GRASP code.[56,57]

TABLE IV. 1*s* ionization potential for Rn (eV).

	Rn (neutral)	Rn (1s hole)	IP (1s)
DC	−642 240.927	−543 260.674	98 980.252
+Breit (SC)	778.104	399.690	−378.414
mag.	891.970	473.801	−418.169
ret.	−94.475	−63.376	31.099
ω-dep.	−19.391	−10.734	8.657
+Breit (PT)	780.425	400.482	−379.943
mag.	894.673	474.767	−419.906
ret.	−94.747	−63.525	31.222
ω-dep.	−19.501	−10.760	8.741
+SE	753.827	482.054	−271.773
+VP	−156.097	−94.204	61.894
Total (SC)	−640 931.677	−542 527.246	98 404.431
Total (PT)	−640 928.327	−542 526.438	98 401.889
Theory			
Indelicato *et al.*[41]			98 408.15
Deslattes *et al.*[42]			98 408.1(28)
Niskanen *et al.*[26]			98 563.2
Experiment			
Bearden and Burr[44]			98 404(14.1)
Deslattes *et al.*[42]			98 404(24)

An atomic state function (ASF) with the total angular momentum J, its z-projection M, and parity p is assumed in the form

$$\Psi_s(JM^p) = \sum_m c_m(s)\Phi(\gamma_m JM^p), \tag{8}$$

where $\Phi(\gamma_m JM^p)$ are configuration state functions (CSFs), $c_m(s)$ are the configuration mixing coefficients for state s, γ_m represents all information required to uniquely define a certain CSF.

The CSF is a Slater determinant of Dirac 4-component bispinors,

$$\Phi(\gamma_m JM^p) = \sum_i d_i \begin{vmatrix} \psi_1(1) & \cdots & \psi_1(N) \\ \vdots & \ddots & \vdots \\ \psi_N(1) & \cdots & \psi_N(N) \end{vmatrix}, \tag{9}$$

where ψ_i is the one-electron wavefunction and d_i coefficients are determined by considering that the CSF is an eigenstate of $\hat{J}^2$ and $\hat{J}_z$. The one-electron wavefunction is defined as

$$\psi = \frac{1}{r}\begin{pmatrix} P_{n,\kappa}(r)\cdot\Omega^{m_j}_{\kappa,j}(\theta,\phi) \\ iQ_{n,\kappa}(r)\cdot\Omega^{m_j}_{-\kappa,j}(\theta,\phi) \end{pmatrix}, \tag{10}$$

TABLE V. SC Breit interaction contribution to the orbital energy for selected atoms (hartree unit).

Z	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
30	0.4364	0.0313	0.0552	0.0359	0.0033	0.0059	0.0031
32	0.5380	0.0394	0.0698	0.0456	0.0039	0.0074	0.0039
36	0.7893	0.0609	0.1074	0.0711	0.0062	0.0123	0.0066
48	2.0170	0.1810	0.3117	0.2109	0.0246	0.0458	0.0274
50	2.3046	0.2105	0.3616	0.2447	0.0291	0.0541	0.0324
54	2.9661	0.2805	0.4794	0.3239	0.0404	0.0747	0.0451
62	4.6759	0.4734	0.8001	0.5359	0.0783	0.1386	0.0855
72	7.6824	0.8271	1.3913	0.9067	0.1482	0.2572	0.1577
80	10.9634	1.2295	2.0673	1.3049	0.2275	0.3933	0.2347
82	11.9291	1.3508	2.2713	1.4201	0.2517	0.4347	0.2571
86	14.0590	1.6247	2.7312	1.6733	0.3084	0.5299	0.3082
104	27.7673	3.5408	5.9576	3.2104	0.7421	1.2328	0.6446
112	36.8476	4.9417	8.3446	4.1270	1.0724	1.7617	0.8494
114	39.5151	5.3734	9.0865	4.3804	1.1751	1.9265	0.9059
118	45.4271	6.3676	10.8087	4.9232	1.4167	2.3132	1.0301
Z	$3d_{3/2}$	$3d_{5/2}$	$4s_{1/2}$	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$
30	0.0002	−0.0008	0.0001				
32	0.0001	−0.0012	0.0001	0.0001	0.0003		
36	0.0008	−0.0016	0.0003	0.0006	0.0001		
48	0.0123	0.0042	0.0035	0.0064	0.0031	0.0001	−0.0009
50	0.0152	0.0057	0.0039	0.0077	0.0036	−0.0001	−0.0014
54	0.0232	0.0102	0.0056	0.0116	0.0055	0.0002	−0.0019
62	0.0535	0.0296	0.0151	0.0277	0.0143	0.0078	−0.0002
72	0.1091	0.0684	0.0302	0.0528	0.0289	0.0142	0.0057
80	0.1708	0.1099	0.0467	0.0834	0.0436	0.0230	0.0096
82	0.1891	0.1220	0.0515	0.0927	0.0476	0.0253	0.0104
86	0.2314	0.1509	0.0646	0.1159	0.0584	0.0324	0.0139
104	0.5273	0.3570	0.1849	0.3096	0.1435	0.0982	0.0551
112	0.7133	0.4841	0.2784	0.4583	0.1938	0.1386	0.0791
114	0.7649	0.5187	0.3071	0.5045	0.2069	0.1491	0.0848
118	0.8791	0.5958	0.3779	0.6161	0.2384	0.1751	0.1005

where $\Omega_{\kappa,j}^{m_j}(\theta,\phi)$ is a angular 2-component spinor and $P_{n,\kappa}(r)$ and $Q_{n,\kappa}(r)$ are the large and small radial parts of the wavefunction, respectively.

B. Computational details

Present results for Breit interaction contribution were obtained by performing calculations with the MCDFGME[53–55] code for the self-consistent approach (using the retarded Breit operator) and by the GRASPK code[57,58] for the perturbational approach (using both retarded and unretarded Breit operators).

The Breit interaction contribution to the orbital energy of the $n\kappa$ subshell has been obtained by the subtraction of the orbital energy computed by means of self-consistent Dirac-Fock equations using the Coulomb operator [only the first part in Eq. (4)], ε^{DC}, from the orbital energy computed by means of self-consistent Dirac-Fock equations using the Coulomb-Breit operator [all parts of Eq. (4)], ε^{DCB}, i.e.,

$$\varepsilon_{n\kappa}^{Breit} = \varepsilon_{n\kappa}^{DCB} - \varepsilon_{n\kappa}^{DC}. \tag{11}$$

III. RESULTS

We first shall compare the Breit contributions to the orbital energy in a many-electron atomic system calculated by a perturbation theory approach and by a self-consistency procedure. Although similar comparisons were presented before in the literature,[16,22] we use experimental data to examine which approach is more accurate. Then we will examine the Z-dependence of Breit contribution to orbital energies. Although the Z-dependence of Breit contribution has been studied in the case of total atomic energy[24] and in the cases of single and double $1s$ electron ionization energies;[26] according to our knowledge, no-one focused on orbital energies. Next, we will study relations between magnetic and retardation parts of the Breit interaction. Finally, we will show results from the DIRAC code[59] for atomic and molecular systems.

TABLE VI. Fitting coefficients for Z-dependence of the Breit interaction (see text for details).

Subshell	a	b	R^2
$1s$	1.370×10^{-6}	3.627	0.999 61
$2s$	1.039×10^{-8}	4.237	0.999 26
$3s$	1.908×10^{-10}	4.761	0.999 42
$4s$	1.709×10^{-12}	5.473	0.999 63
$2p_{1/2}$	1.557×10^{-8}	4.263	0.999 08
$3p_{1/2}$	6.649×10^{-9}	4.601	0.999 37
$4p_{1/2}$	9.472×10^{-12}	5.216	0.999 63
$2p_{3/2}$	3.836×10^{-7}	3.431	0.999 97
$3p_{3/2}$	1.201×10^{-8}	3.830	0.999 88
$4p_{3/2}$	2.109×10^{-10}	4.372	0.999 45

A. Breit contributions from perturbational and self-consistent procedures

The comparison between perturbational (PT) and self-consistent field (SC) computational approaches of the Breit interaction energy contribution per subshell is presented in Tables I and II. The PT numbers are presented in the case

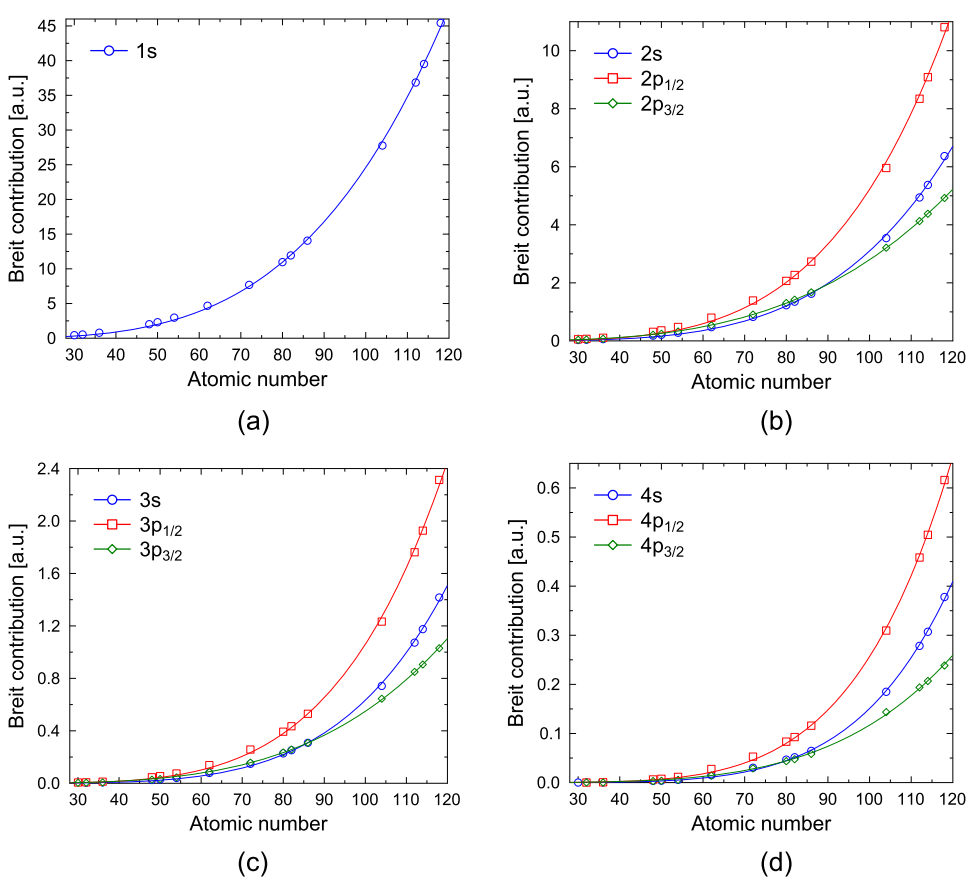

FIG. 1. Breit contributions to Dirac-Coulomb orbital energy for nl subshells (points) and fit lines to them.

of frequency-dependent Breit operator, "PT," and in the case of frequency-independent Breit operator, "PT*." Our results of the Breit contributions to the orbital energies for the Hg atom are similar to the studies by Lindroth *et al.*,[16] by Thierfelder and Schwerdtfeger,[22] by Mann and Johnson,[24] and by Parpia *et al.*[27] in each, SC, PT, and PT* case. We also performed similar calculations for Zn, Xe, and No, in order to have more comprehensive insights into PT vs SC treatment of the Breit contributions. As one can see from Tables I and II, our results are very close to the data presented in the literature,[12,16,22,24,27,28] for both PT and SC approaches. The PT contribution is higher than the SC one in all studied cases. The PT-SC difference decreases when Z increases (from 10% for 1s of Zn to 5% for 1s of No) and increases rapidly when the shell number n of orbital increases (no case: 5% for 1s, 20% for 2s, and 43% for 3s). However, if changes of atomic (or molecular) orbitals due to the Breit term (see, e.g., Ref. 60) are considered, a variational self-consistent treatment is required. As one can see, the finite ω corrections contribute to the orbital Breit energy contribution more in the case of $p_{3/2}$ orbital than in the case of s or $p_{1/2}$ orbitals, but all do not exceed ~10%–compared to columns "PT" and "PT*" in Tables I and II.

In order to keep track on how accurate our results are as compared with experiments, we performed the calculation of 1s ionization potential of Xe and Rn, which were recently studied by Niskanen *et al.*[26] and by Barysz and Syrocki;[43]–see Tables III and IV. The "DC" (Dirac-Coulomb energy only), "Breit (SC)," "Breit (PT)," "SE" (in the Welton model), and "VP" (Uehling potential) are contributions calculated by the MCDFGME code. Total values also include higher order SE and VP terms by means of the MCDFGME code.[2] The "total (SC)" means "DC" + "Breit (SC)" + "SE" + "VP" + higher order contributions. The "total (PT)" is similar to the "total (SC)," but the "Breit (SC)" contribution is replaced by the "Breit (PT)" contribution. The Breit correction is divided into three contributions: "mag."—magnetic (Gaunt) part, "ret."—frequency independent retardation part [V_{ret} in Eqs. (7)], and "ω-dep."—frequency dependent retardation part. As one can see from Table III, our "total (SC)" results are even closer to the experiment than very accurate result of Indelicato *et al.*[41] and Deslattes *et al.*[42] (both obtained using the earlier version of the MCDFGME code and SC treatment of the Breit term). The "total (PT)" values are only a little farther away from the experiment but still in very good agreement. Then we decided to use SC Breit values in our study. One can see that the difference between SC and PT results is bigger in the case of orbital energies (see Tables I and II) than in the case of total state energies.

B. Z-dependence of Breit contribution

In Table V, the contribution of the Breit interaction to the orbital energy for selected atoms with $30 \le Z \le 118$ has been collected. Their Z-dependencies have been examined by fitting Breit contributions to the orbital ns (n = 1–4) and $n'p_{1/2}$ and $n'p_{3/2}$ (n' = 2–4) energies, with the function

$$\varepsilon_{nl}^{Breit}(Z) = a \times Z^b. \tag{12}$$

TABLE VII. Breit energy contributions to the Dirac-Coulomb orbital energy ratio (all numbers are multiplied by 10^3, e.g., −1.2199 means -1.2199×10^{-3}).

Z	$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
30	−1.2199	−0.6901	−1.3901	−0.9229	−0.5691	−1.4896	−0.8170
32	−1.3088	−0.7372	−1.4749	−0.9879	−0.5299	−1.3990	−0.7568
36	−1.4901	−0.8450	−1.6562	−1.1309	−0.5513	−1.4220	−0.7896
48	−2.0428	−1.2085	−2.2417	−1.5989	−0.8404	−1.8356	−1.1599
50	−2.1353	−1.2657	−2.3351	−1.6720	−0.8664	−1.8754	−1.1900
54	−2.3223	−1.3856	−2.5275	−1.8229	−0.9404	−1.9844	−1.2772
62	−2.7010	−1.6492	−2.9480	−2.1507	−1.2110	−2.3936	−1.6051
72	−3.1793	−1.9782	−3.4920	−2.5576	−1.5208	−2.8988	−1.9923
80	−3.5662	−2.2344	−3.9238	−2.8668	−1.7092	−3.2072	−2.2026
82	−3.6639	−2.2978	−4.0311	−2.9411	−1.7512	−3.2739	−2.2442
86	−3.8611	−2.4293	−4.2520	−3.0924	−1.8486	−3.4214	−2.3398
104	−4.7804	−3.0857	−5.3620	−3.7923	−2.4394	−4.2899	−2.8778
112	−5.2121	−3.4207	−5.9364	−4.0979	−2.7444	−4.7360	−3.0890
114	−5.3235	−3.5113	−6.0922	−4.1724	−2.8257	−4.8555	−3.1350
118	−5.5518	−3.7062	−6.4278	−4.3241	−3.0077	−5.1213	−3.2359
Z	$3d_{3/2}$	$3d_{5/2}$	$4s_{1/2}$	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$
30	−0.2611	1.0941	−0.4185				
32	−0.0931	0.7722	−0.2056	−0.3897	−0.8719		
36	−0.2054	0.4273	−0.2112	−1.0382	−0.1307		
48	−0.7692	−0.2648	−0.7334	−1.9520	−1.0293	−0.1144	1.2454
50	−0.7986	−0.3015	−0.6649	−1.8076	−0.9214	0.0574	1.0821
54	−0.8897	−0.3983	−0.6675	−1.7911	−0.9272	−0.0847	0.7250
62	−1.2821	−0.7275	−1.1044	−2.5216	−1.4420	−1.3927	0.0305
72	−1.6867	−1.0922	−1.4554	−3.0769	−1.9363	−1.5775	−0.6668
80	−1.9100	−1.2773	−1.5222	−3.1913	−1.9645	−1.5526	−0.6803
82	−1.9537	−1.3133	−1.5177	−3.1773	−1.9320	−1.5007	−0.6462
86	−2.0557	−1.4004	−1.5634	−3.2186	−1.9383	−1.5045	−0.6798
104	−2.6611	−1.9148	−2.1807	−4.0296	−2.4267	−2.1017	−1.2615
112	−2.9010	−2.1103	−2.4541	−4.3971	−2.5376	−2.2324	−1.3741
114	−2.9533	−2.1512	−2.5182	−4.4847	−2.5440	−2.2401	−1.3770
118	−3.0668	−2.2427	−2.6814	−4.7027	−2.5905	−2.2962	−1.4291

Coefficients a and b have been collected in Table VI (also R^2 fitting parameters have been presented). The fitting has been performed by means of the Nelder-Mead simplex algorithm implemented in the SciDAVis program.[61]

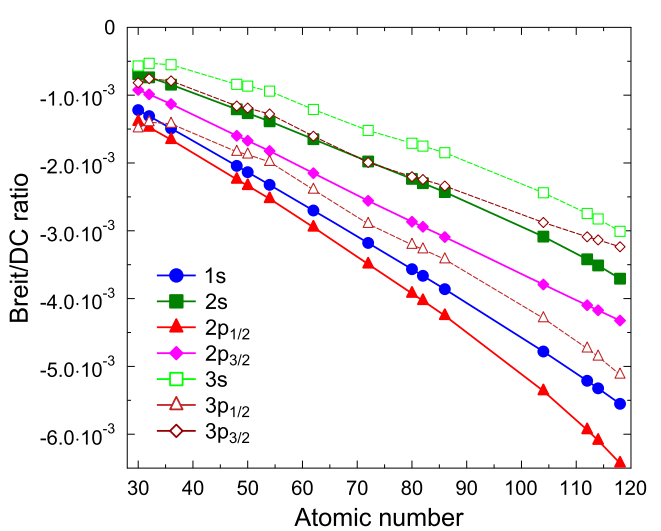

FIG. 2. Breit energy contributions to the Dirac-Coulomb orbital energy ratio for selected subshells.

TABLE VIII. Magnetic (Gaunt) and retardation parts of Breit contributions to the Dirac-Coulomb orbital energy for selected atoms (hartree unit).

Z		$1s_{1/2}$	$2s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$	$3s_{1/2}$	$3p_{1/2}$	$3p_{3/2}$
10	mag.	1.13×10^{-2}	1.79×10^{-4}	4.40×10^{-4}	7.11×10^{-5}			
	ret.	-5.40×10^{-5}	4.13×10^{-5}	-3.23×10^{-5}	-3.22×10^{-5}			
18	mag.	8.44×10^{-2}	3.73×10^{-3}	7.82×10^{-3}	4.60×10^{-3}	1.30×10^{-4}	3.54×10^{-4}	5.81×10^{-5}
	ret.	-3.32×10^{-3}	1.07×10^{-4}	-7.56×10^{-4}	-7.55×10^{-4}	3.09×10^{-5}	-3.14×10^{-5}	-3.14×10^{-5}
36	mag.	0.8417	0.0634	0.1204	0.0841	6.24×10^{-3}	1.38×10^{-2}	8.09×10^{-3}
	ret.	−0.0524	−0.0025	−0.0130	−0.0129	-5.10×10^{-5}	-1.54×10^{-3}	-1.53×10^{-3}
54	mag.	3.1910	0.3006	0.5393	0.3836	4.25×10^{-2}	8.38×10^{-2}	5.41×10^{-2}
	ret.	−0.2249	−0.0201	−0.0599	−0.0597	-2.06×10^{-3}	-9.03×10^{-3}	-9.01×10^{-3}
86	mag.	15.1617	1.7830	3.0421	1.9849	0.3393	0.5894	0.3678
	ret.	−1.1027	−0.1583	−0.3109	−0.3116	−0.0309	−0.0594	−0.0596
118	mag.	48.5109	7.1312	11.6743	5.8557	1.6143	2.5255	1.2324
	ret.	−3.0836	−0.7636	−0.8656	−0.9325	−0.1976	−0.2123	−0.2023
Z		$3d_{3/2}$	$3d_{5/2}$	$4s_{1/2}$	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$
36	mag.	5.79×10^{-4}	-1.79×10^{-3}	1.96×10^{-4}	6.17×10^{-4}	1.22×10^{-4}		
	ret.	1.97×10^{-4}	1.97×10^{-4}	5.45×10^{-5}	-5.49×10^{-5}	-5.52×10^{-5}		
54	mag.	2.47×10^{-2}	1.16×10^{-2}	5.79×10^{-3}	1.30×10^{-2}	6.99×10^{-3}	5.90×10^{-5}	-2.08×10^{-3}
	ret.	-1.52×10^{-3}	-1.48×10^{-3}	-1.65×10^{-4}	-1.45×10^{-3}	-1.44×10^{-3}	1.71×10^{-4}	1.69×10^{-4}
86	mag.	0.2581	0.1767	0.0715	0.1295	0.0713	0.0360	0.0173
	ret.	−0.0267	−0.0258	−0.0069	−0.0135	−0.0129	−0.0036	−0.0034
118	mag.	0.9922	0.7029	0.4332	0.6752	0.2892	0.1959	0.1204
	ret.	−0.1131	−0.1070	−0.0553	−0.0591	−0.0508	−0.0207	−0.0199
Z		$4f_{5/2}$	$4f_{7/2}$	$5s_{1/2}$	$5p_{1/2}$	$5p_{3/2}$	$5d_{3/2}$	$5d_{5/2}$
54	mag.			2.29×10^{-4}	8.22×10^{-4}	1.63×10^{-4}		
	ret.			6.05×10^{-5}	-6.91×10^{-5}	-6.99×10^{-5}		
86	mag.	-9.87×10^{-3}	-1.81×10^{-2}	1.10×10^{-2}	2.12×10^{-2}	8.96×10^{-3}	1.31×10^{-4}	-2.63×10^{-3}
	ret.	2.76×10^{-3}	2.74×10^{-3}	-8.48×10^{-4}	-2.02×10^{-3}	-1.93×10^{-3}	1.82×10^{-4}	1.75×10^{-4}
118	mag.	3.18×10^{-2}	-3.54×10^{-3}	0.1150	0.1796	0.0642	3.21×10^{-2}	1.27×10^{-2}
	ret.	2.07×10^{-3}	2.15×10^{-3}	−0.0143	−0.0148	−0.0128	-3.46×10^{-3}	-3.37×10^{-3}
Z		$5f_{5/2}$	$5f_{7/2}$	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$
86	mag.			6.64×10^{-4}	1.70×10^{-3}	1.94×10^{-4}		
	ret.			4.01×10^{-5}	-9.73×10^{-5}	-9.84×10^{-5}		
118	mag.	-1.20×10^{-2}	-1.94×10^{-2}	2.41×10^{-2}	3.85×10^{-2}	8.49×10^{-3}	-2.30×10^{-5}	-3.01×10^{-3}
	ret.	2.52×10^{-3}	2.47×10^{-3}	-2.62×10^{-3}	-2.47×10^{-3}	-2.07×10^{-3}	2.14×10^{-4}	1.79×10^{-4}
Z		$7s_{1/2}$	$7p_{1/2}$	$7p_{3/2}$				
118	mag.	2.67×10^{-3}	4.60×10^{-3}	8.30×10^{-5}				
	ret.	-1.49×10^{-4}	-9.87×10^{-5}	-1.03×10^{-4}				

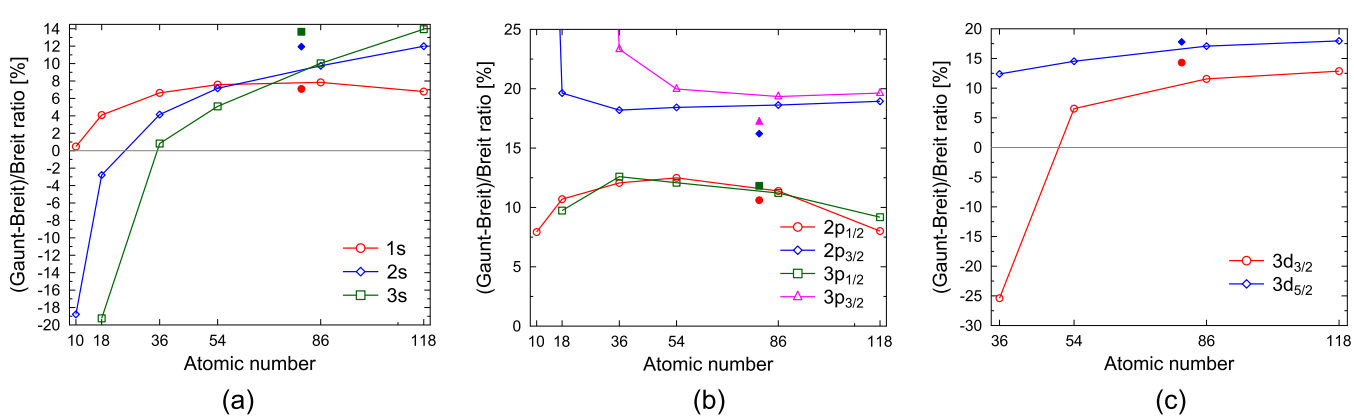

FIG. 3. Percentage difference of full Breit vs Gaunt contributions to the Dirac-Coulomb orbital energy for nl ($n \leq 3$) subshells. Results from the work of Mann and Johnson[24] are presented by filled markers.

TABLE IX. Gaunt contribution to the energy of molecular levels for HX systems, where X = Br, I, At, and the equivalent isoelectronic atomic systems (hartree unit). MO = molecular orbital and AO = atomic orbital.

		Dirac		Mcdfgme		Dirac		Mcdfgme		Dirac		Mcdfgme	
MO	AO	HBr	Kr	Br	Kr	HI	Xe	I	Xe	HAt	Rn	At	Rn
1	1s	0.7673	0.8417	0.7673	0.8417	3.000	3.191	3.000	3.191	14.574	15.176	14.561	15.162
2	2s	0.0570	0.0634	0.0570	0.0634	0.280	0.301	0.280	0.300	1.704	1.785	1.702	1.783
3	$2p_{1/2}$	0.1086	0.1204	0.1086	0.1204	0.504	0.539	0.504	0.539	2.911	3.045	2.908	3.042
4	$2p_{3/2}$	0.0756	0.0841	0.0756	0.0841	0.358	0.384	0.358	0.384	1.908	1.986	1.907	1.985
5	$2p_{3/2}$	0.0756	0.0841	0.0756	0.0841	0.359	0.384	0.358	0.384	1.908	1.986	1.907	1.985
6	3s	0.0056	0.0062	0.0056	0.0062	0.0390	0.0430	0.0392	0.0425	0.323	0.340	0.322	0.339
7	$3p_{1/2}$	0.0122	0.0138	0.0122	0.0138	0.0780	0.0840	0.0775	0.0838	0.562	0.590	0.561	0.589
8	$3p_{3/2}$	0.0071	0.0081	0.0071	0.0081	0.0500	0.0540	0.0500	0.0541	0.352	0.368	0.352	0.368
9	$3p_{3/2}$	0.0071	0.0081	0.0071	0.0081	0.0500	0.0540	0.0500	0.0541	0.352	0.368	0.352	0.368
10	$3d_{3/2}$	3.57×10^{-4}	5.81×10^{-4}	3.57×10^{-4}	5.79×10^{-4}	0.0220	0.0247	0.0223	0.0247	0.246	0.258	0.246	0.258
11	$3d_{3/2}$	3.48×10^{-4}	5.81×10^{-4}	3.57×10^{-4}	5.79×10^{-4}	0.0220	0.0247	0.0223	0.0247	0.246	0.258	0.246	0.258
12	$3d_{5/2}$	-1.71×10^{-3}	-1.79×10^{-3}	-1.73×10^{-3}	-1.79×10^{-3}	0.0102	0.0117	0.0102	0.0116	0.168	0.177	0.168	0.177
13	$3d_{5/2}$	-1.71×10^{-3}	-1.79×10^{-3}	-1.73×10^{-3}	-1.79×10^{-3}	0.0102	0.0117	0.0102	0.0116	0.168	0.177	0.168	0.177
14	$3d_{5/2}$	-1.72×10^{-3}	-1.79×10^{-3}	-1.73×10^{-3}	-1.79×10^{-3}	0.0102	0.0117	0.0102	0.0116	0.168	0.177	0.168	0.177
15	4s	1.38×10^{-4}	1.98×10^{-4}	1.61×10^{-4}	1.96×10^{-4}	0.0053	0.0060	0.0053	0.0058	0.0676	0.0716	0.0675	0.0715
16	$4p_{1/2}$	1.08×10^{-4}	6.19×10^{-4}	4.93×10^{-4}	6.17×10^{-4}	0.0118	0.0130	0.0118	0.0130	0.1227	0.1296	0.1226	0.1295
17	$4p_{3/2}$	3.24×10^{-4}	1.24×10^{-4}	9.0×10^{-5}	1.22×10^{-4}	0.0063	0.0070	0.0063	0.0070	0.0679	0.0713	0.0678	0.0713
18	$4p_{3/2}$	7.7×10^{-5}	1.24×10^{-4}	9.0×10^{-5}	1.22×10^{-4}	0.0063	0.0070	0.0063	0.0070	0.0679	0.0713	0.0678	0.0713
19	$4d_{3/2}$					-4.1×10^{-5}	6.3×10^{-5}	-4.7×10^{-5}	5.9×10^{-5}	0.0340	0.0361	0.0339	0.0360
20	$4d_{3/2}$					-4.7×10^{-5}	6.3×10^{-5}	-4.7×10^{-5}	5.9×10^{-5}	0.0340	0.0361	0.0339	0.0360
21	$4d_{5/2}$					-1.94×10^{-3}	-2.08×10^{-3}	-1.96×10^{-3}	-2.08×10^{-3}	0.0162	0.0173	0.0162	0.0173
22	$4d_{5/2}$					-1.94×10^{-3}	-2.08×10^{-3}	-1.96×10^{-3}	-2.08×10^{-3}	0.0162	0.0173	0.0162	0.0173
23	$4d_{5/2}$					-1.95×10^{-3}	-2.08×10^{-3}	-1.96×10^{-3}	-2.08×10^{-3}	0.0162	0.0173	0.0162	0.0173
24	$4f_{5/2}$									−0.0097	−0.0181	−0.0097	−0.0099
25	$4f_{5/2}$									−0.0097	−0.0181	−0.0097	−0.0099
26	$4f_{5/2}$									−0.0097	−0.0181	−0.0097	−0.0099
27	$4f_{7/2}$									−0.0175	0.0087	−0.0175	−0.0181
28	$4f_{7/2}$									−0.0175	0.0087	−0.0175	−0.0181
29	$4f_{7/2}$									−0.0175	0.0087	−0.0175	−0.0181
30	$4f_{7/2}$									−0.0175	0.0087	−0.0175	−0.0181
31	5s					1.65×10^{-4}	2.31×10^{-4}	1.91×10^{-4}	2.29×10^{-4}	0.0102	0.0110	0.0102	0.0110
32	$5p_{1/2}$					1.81×10^{-4}	8.24×10^{-4}	6.80×10^{-4}	8.22×10^{-4}	0.0196	−0.0099	0.0196	0.0212
33	$5p_{3/2}$					4.38×10^{-4}	1.65×10^{-4}	1.31×10^{-4}	1.63×10^{-4}	0.0083	−0.0099	0.0083	0.0090
34	$5p_{3/2}$					1.20×10^{-4}	1.65×10^{-4}	1.31×10^{-4}	1.63×10^{-4}	0.0083	−0.0099	0.0083	0.0090
35	$5d_{3/2}$									1×10^{-6}	1.33×10^{-4}	$<1\times10^{-6}$	1.31×10^{-4}
36	$5d_{3/2}$									2×10^{-6}	1.33×10^{-4}	$<1\times10^{-6}$	1.31×10^{-4}
37	$5d_{5/2}$									-2.49×10^{-3}	-2.63×10^{-3}	-2.50×10^{-3}	-2.63×10^{-3}
38	$5d_{5/2}$									-2.50×10^{-3}	-2.63×10^{-3}	-2.50×10^{-3}	-2.63×10^{-3}

TABLE IX. (*Continued.*)

		Dirac			McDFGME			Dirac			McDFGME			Dirac		McDFGME	
MO	AO	HBr	Kr	Br	Kr	HI	Xe	I	Xe	HAt	Rn	At	Rn
39	$5d_{5/2}$									-2.50×10^{-3}	-2.63×10^{-3}	-2.50×10^{-3}	-2.63×10^{-3}
40	6s									5.01×10^{-4}	6.66×10^{-4}	5.50×10^{-4}	6.64×10^{-4}
41	$6p_{1/2}$									7.32×10^{-4}	1.71×10^{-3}	1.43×10^{-3}	1.70×10^{-3}
42	$6p_{3/2}$									5.71×10^{-4}	1.95×10^{-4}	1.52×10^{-4}	1.94×10^{-4}
43	$6p_{3/2}$									1.43×10^{-4}	1.95×10^{-4}	1.52×10^{-4}	1.94×10^{-4}

New insights appear. The Z-dependence is different for different shells even though the pattern of grow is similar in all cases. There is an increase of b coefficient when n increase, being its range of 3.627-5.473 for ns subshells, of 4.263-5.216 for $np_{1/2}$ subshells, and of 3.431-4.372 for $np_{3/2}$ subshells. The pattern of the relationship among $ns_{1/2}$, $np_{1/2,}$ and $np_{3/2}$ is such that (i) the a coefficient of $np_{3/2}$ is one order of magnitude larger than the other two (which are of the same order of magnitude); (ii) for given n, the b coefficients for $np_{3/2}$ are smaller than those for $ns_{1/2}$ and $np_{1/2}$ (see Table VI). This can be seen in Figs. 1(b)–1(d).

In both Table VII and Fig. 2, the Breit energy contributions to Dirac-Coulomb orbital energy ratios ($R^{B/DC}$) for selected subshells are presented. It is clearly seen that the absolute value of the $R^{B/DC}$ ratio (as the Breit energy contribution has opposite sign than the Dirac-Coulomb orbital energy) increases when Z increases. For given n, the following trend appears: $\mathrm{abs}(R^{B/DC}_{np_{1/2}}) > \mathrm{abs}(R^{B/DC}_{np_{3/2}}) > \mathrm{abs}(R^{B/DC}_{ns_{1/2}})$. For 1$s$ subshell, the $R^{B/DC}$ ratio scales as $\sim Z^{1.1}$, what confirms the finding of Niskanen *et al.*[26] for single and double 1s electron ionization energies of noble gases.

C. Gaunt vs retardation contribution

We analyze here results of calculations performed with the McDFGME code for Gaunt and full-Breit (i.e., a sum of Gaunt and retardation contributions) energy contributions for different subshells. In Table VIII, the magnetic (Gaunt) and retardation parts of Breit contributions to the Dirac-Coulomb orbital energy for nl ($n = 1$–3, $l = 0$–2) orbitals of selected atoms have been collected. In Fig. 3, we show what kind of relationship both contributions to the orbital energies do follow. It is clearly seen that the full-Breit terms are smaller than the Gaunt ones, except the results for valence shells. That is because usually the Gaunt term and the retardation term have opposite signs. Considering only inner shells, the retardation term contributes to the full-Breit term about 10% for ns and $nl_{l-1/2}$ (i.e., $np_{1/2}$ and $nd_{3/2}$) subshells, and about 20% for $nl_{l+1/2}$ (i.e., $np_{3/2}$ and $nd_{5/2}$) subshells. For 1s shell, which is the most important one contributing to the total energy of any atomic system, the difference between Gaunt and full-Breit contributions is almost constant for high-Z atoms and is about 7%-8%. Our numbers are in agreement with the results of Lindroth *et al.*,[16] that the retardation part gives 5-10% contribution to the Breit interaction for the heavier elements. They are also in agreement with the finding of Indelicato,[51] that the retardation part has opposite sign and is about 2-10% of magnetic part for 1s binding energy of Ne-like and Rn-like ions of superheavy elements (Z = 100–172). Mann and Johnson[24] studied frozen-orbital binding energies (which are equivalent to orbital energies) of Hg and the values of Gaunt vs. full-Breit difference. Their findings are close to ours, though they are bigger in the case of ns ($n \geq 2$) subshells. Recently, Niskanen *et al.*[26] found that the Gaunt vs. full-Breit difference is about 3%-7% in the case of 1s single ionization energies of noble gases (Ne to Rn), and 5%-11% in the case of their 1s double ionization energies. We found that for valence $np_{3/2}$ subshells the Gaunt and retardation contributions are of comparable size. It is worth to note that for some outer (valence or near to valence)

s- or *d*-type orbitals the retardation part of Breit correction has the same sign as the magnetic part. This same finding has been found by Huang *et al.*[25] for relaxed-orbital binding energies.

D. Gaunt contribution for molecular orbitals

The Gaunt contributions to Kr, Xe, and Rn noble gases and its iso-electronic HBr, HI, and HAt diatomic molecules (calculated by using Dirac code) are presented in Table IX. The atomic calculations for Br, I, At, Kr, Xe, and Rn, performed with the Mcdfgme code, are also presented for comparison. Note that for $j > 1/2$, the degeneration of nl_j atomic levels is reduced in the HX molecule because of axial symmetry. The Z-dependence of Gaunt, as well as Breit, contribution to the orbital energy can be approximated by a power function, being the exponent about 4-5. For inner subshells, where molecular orbitals of HX (X = Br, I, At) diatomic system are very similar to the atomic orbitals of the X atom, the Gaunt contribution to the energy of the *nl* atomic orbital of noble gas is always larger than the Gaunt contribution to the energy of the corresponding molecular orbital of the HX molecule. For this case, the exponential Z-dependence of Gaunt/Breit contribution is clearly visible. For outer subshells, where molecular orbitals of the HX diatomic system are far from atomic orbitals of the X atom, the Gaunt contribution to the energy of the *nl* atomic orbital of noble gas may be smaller or higher or may be of opposite sign than the Gaunt contribution to the energy of the corresponding molecular orbital of the HX molecule.

IV. CONCLUSIONS

In this study, we investigated Breit effects (magnetic and retarded) on individual atomic and molecular orbital energies. Based on the findings presented above, a few main conclusions can be drawn.

(1) We can state that both frequency-dependent self-consistent and perturbational approaches to calculate the Breit energy contribution provide accurate results. This was validated by their comparison with experiments on the 1*s* ionization potential for Xe and Rn. However, in the case of Rn 1*s* ionization potential, the self-consistent approach to calculate the Breit energy contribution seems to be a little more accurate.

(2) The Z-dependence of Breit contribution to orbital energies has been evaluated by fitting Breit contributions to the orbital *ns* and *np* energies by $a \times Z^b$ power function. The *a* and *b* coefficients may be used to estimate Breit effects on inner molecular orbitals. We observe some clean patterns: (i) for given *n*, $\varepsilon^B_{np_{1/2}} > \varepsilon^B_{np_{3/2}}$ and $\varepsilon^B_{np_{1/2}} > \varepsilon^B_{ns}$; (ii) $\varepsilon^B_{ns} < \varepsilon^B_{np_{3/2}}$ for $Z \lesssim 80$–90 ($Z < 91$ for $n = 2$ and $Z < 86$ for $n = 3$) but opposite dependence for higher Z.

(3) We found that the retardation part contributes to the full-Breit term below 8% in the case of 1*s* orbital energy but larger (≃20% or even more) for outer subshells.

(4) Comparison between the Gaunt term energy contribution per molecular level of HX systems (where X = $_{35}$Br, $_{53}$I, $_{85}$At) and per atomic orbital of the equivalent isoelectronic atomic systems ($_{35}$Kr, $_{54}$Xe, $_{86}$Rn) shows that (i) for inner orbitals the Gaunt contributions to molecular systems are close to that of atomic systems, and (ii) for outer orbitals these contributions to molecular orbitals cannot be accurately reproduced by the corresponding atomic contributions.

For valence shells, the retardation term is a major part of the Breit interaction; therefore, there is a need for more study on Breit corrections to molecular level energies. We hope that our work will stimulate to implement the retardation term of the Breit interaction in leading molecular codes, such as the Dirac code.

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