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Effect of removing the no-virtual-pair approximation on the correlation energy of the He isoelectronic sequence

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The correlation energies (CEs) for the He-like ions are studied with the virtual-pair approximation (VPA) and with the no-virtual-pair approximation (NVPA). In contrast to the nonrelativistic CEs, the CEs calculated with relativity fell sharply as the nuclear charge Z increased, although the CE calculated with the NVPA was considerably lower than with the VPA for the heavier atoms. It is shown that CE calculated with a Hylleraas-type function implicitly includes the effects of the excitations into negative-energy states, which corresponds to the VPA. The present results verify that the strong dependence on Z of the CE of He-like ions is an essential effect of the relativity.

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I. INTRODUCTION

The nonrelativistic correlation energy $CE(\text{nonrel})$ is almost constant at -0.045 hartrees for He-like ion atoms heavier than ${}_6\text{C}$,¹⁻⁴ where

$$CE(\text{nonrel}) = TE(\text{nonrel:correlated}) - TE(\text{RHF}), \quad (1)$$

and $TE(\text{correlated})$ and $TE(\text{RHF})$ correspondingly denote the total energies (TEs) calculated with electronic correlation included and with restricted Hartree-Fock (RHF). In contrast, the relativistic correlation energy $CE(\text{rel})$,

$$CE(\text{rel}) = TE(\text{rel:correlated}) - TE(\text{DF}), \quad (2)$$

depends strongly on the nuclear charge Z , where DF denotes a Dirac-Fock calculation.

Pestka and Karwowski^{5,6} showed, using the Hylleraas-type configuration interaction (CI) method, that $CE(\text{rel})$ has a minimum of -0.046 hartrees at ${}_{20}\text{Ca}$, a maximum of -0.045 hartrees at ${}_{68}\text{Er}$, then decreases rapidly. It reaches -0.063 hartrees for the atom having $Z=116$. They first suggested that this curious behavior of $CE(\text{rel})$ arises from a small numerical error in calculating the Hamiltonian matrix elements, which might violate the condition for Hylleraas-Undheim-McDonald theorem.^{7,8} They also pointed out that Hylleraas-type functions do not satisfy kinetic balance conditions needed to guarantee the boundary properties of the Hamiltonian matrix.^{9,10} Multireference-DF (MRDF) spinors are considered to satisfy kinetic balance, giving no artificial error in solving the Hamiltonian eigenvalue problem. Recently, Pestka *et al.*¹¹ have shown that the $CE(\text{rel})$ value given by MRDF [denoted as $CE(\text{MRDF})$] has the same ten-

dency as the Hylleraas-type CI, $CE(\text{Hylleraas})$. By using near-complete basis sets of s , p , d , and f primitive Gaussian-type functions (pGTFs) and positive-energy spinors in the Dirac-Fock-Roothaan (DFR) method, Watanabe and Tatewaki¹² also investigated $CE(\text{rel})$ [denoted as $CE(\text{NVPA:spdf})$]. Here we call the correlated calculation with positive-energy spinors the no-virtual-pair approximation (NVPA) or simply the no-pair approximation,¹³⁻¹⁸ and call the correlation calculations using both positive- and negative-energy spinors the virtual-pair approximation (VPA) or simply the pair approximation. Two calculations^{11,12} with NVPA confirmed the results of the earlier investigations by Pestka and Karwowski.^{5,6} However, it was found that $CE(\text{NVPA:spdf})$ and even $CE(\text{MRDF})$ exceed $CE(\text{Hylleraas})$ in some heavier atoms; for example, $CE(\text{NVPA:spdf})$ overtakes $CE(\text{Hylleraas})$ at ${}_{38}\text{Sr}$.

In the present paper, we clarify why $CE(\text{NVPA:spdf})$ and $CE(\text{MRDF})$ surpass $CE(\text{Hylleraas})$. Since the s -, p -, d -, and f -CI¹² calculation was considered to be near to the CI limit in the NVPA, we added to this CI space the configuration state function (CSF) which includes the excitations into negative energy, which is equivalent to the VPA. We shall see that removal of the NVPA is crucial in considering the correlation effects in He-like ions, suggesting the need to reconsider the NVPA in the treatment of molecules including heavy atoms.

In DFR calculations we performed self-consistent-field calculations under the use of the Dirac-Coulomb Hamiltonian and the basis sets for the large and small components, and then throw out the lower half solutions including the negative-energy spinors. We performed a similar treatment in the CI calculations: first, we perform the full CI calculation for two particle state under the Dirac-Coulomb Hamiltonian, using all the basis sets for the large and small components.

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Then we throw out the solutions including the negative-energy spinors and get the correlated states including the positive-energy spinors. In the present case the TE dependence on the choice of the external potentials found in NVPA disappears.^{19,20} The effects from the negative sea is beyond the scope of the present work. The discussion related to this is given by Saue and Visscher.²⁰

The importance of the VPA is also discussed in connection with the transition probabilities; the contribution of CSFs with negative-energy spinor is considered, since the transition probabilities become gauge-dependent unless these CSFs are incorporated.^{21,22} Contributions of the negative-energy states for TEs of He-like ions have been discussed by several authors.^{19,23–25} We shall compare the present results with those of previous papers.

Section II sets out the method of calculation, including the basis set and the CI scheme. Section III discusses the characteristics of the diagonal terms of the Hamiltonian matrix, including the lowest diagonal term of the positive energies and the highest diagonal term of the negative energies, and also discusses the effect of removing the NVPA, considering partial electron correlations from $s's''$, $p'p''$, $d'd''$, and $f'f''$ shells. Section IV gives our conclusions.

II. METHOD OF CALCULATION

We use the Dirac-Coulomb Hamiltonian, where the uniform charge sphere model is used for the nucleus. Throughout the paper we adopt the atomic unit. We consider the correlation energies of the He-like ions up to $Z=116$. An accurate basis set is needed to give the numerical Dirac-Fock (NDF) limit, since we consider the correlation energy defined by Eq. (2). Use of the individual basis sets for the individual atoms is tedious. Following previous work,¹² we therefore used a universal set composed of 80 primitive s -type pGTFs, with their exponents determined by a geometric sequence,

$$\zeta_n = \alpha\beta^{n-1} \quad (\alpha = 0.005\,88, \beta = 1.493\,320, \\ n = 1, \dots, 80). \quad (3)$$

The largest and smallest exponents are $3.368\,581\,44E+11$ and $5.88E-03$. One may interest in comparing the largest exponent with the exponents of the radii of the uniform charge sphere nucleus model of Visscher and Dyall.²⁶ These take $2.12E+09 \sim 1.19E+08$ for the atoms ${}_1\text{H} \sim {}_{109}\text{Mt}$ which are two or three order smaller than that of largest exponent of the present basis. We performed the DFR and CI calculations, using the SCF (Ref. 27) and CI (Refs. 28 and 29) programs written by Matsuoka and Watanabe.

This set gives exact DFR TEs for ${}_2\text{He}$ to ${}_{120}\text{Ubn}^{118+}$, where, for example, DFR TEs for ${}_{80}\text{Hg}(202)^{78+}$, ${}_{100}\text{Fm}(257)^{98+}$, and ${}_{120}\text{Ubn}(294)^{118+}$ are, respectively, $-7002.455\,714\,92$, $-11\,763.984\,089\,90$, and $-18\,973.261\,226\,40$ hartrees. The errors ΔTE , defined by

$$\Delta\text{TE} = \text{TE}(\text{DFR}) - \text{TE}(\text{NDF}), \quad (4)$$

are less than $0.01\,\mu\text{hartrees}$. Since a previous calculation¹² has shown that CE dependence on Z is mainly due to $s^2 \rightarrow s's''$ transitions, and since computer resources are finite,

TABLE I. Spinor energies (ϵ) and TEs for He, Xe^{52+} , and Uuh^{114+} (in hartrees).

	He	Xe^{52+}	Uuh^{114+}
$\epsilon(p80s)$	319 137 896.505	318 515 047.835	318 037 141.079
$\text{TE}(p80s^2)$	638 735 720.571	637 489 793.039	636 533 372.930
$\epsilon(p1s)$	-0.918	-1 483.656	-8 571.002
$\text{TE}(p1s^2)$	-2.862	-3 002.946	-17 250.673
$\epsilon(n80s)$	-37 557.729	-37 559.706	-37 562.049
$\text{TE}(n80s^2)$	-75 115.598	-75 119.527	-75 124.15
$\epsilon(n1s)$	-319 304 832.807	-319 927 681.408	-320 405 588.172
$\text{TE}(n1s^2)$	-638 149 740.792	-639 395 672.259	-640 352 067.268

we first examine the correlation effects of these excitations, using all the resulting DFR spinors: we have 160 spinors, 80 positive and 80 negative ones. We perform NVPA-CI and VPA-CI calculations, whose CI dimensions are, respectively, 6400 and 25 600. It emerges that VPA is very important, and we therefore also take into account the angular correlation effect.

It is desirable to use the same set as s for other symmetries. However, if we use 80 pGTFs for the respective sub-symmetries of the p , d , and f spinors as for s , then the numbers of the pGTFs are 480, 800, and 1120 for the p , d , and f spinors (see Sec. III C). The same CI calculation as for the s spinors including all the pGTFs is huge. We select the pGTFs for the CI calculations according to the spinor coefficients of DFR. The number of selected pGTFs is 400–600. Although it is desirable to treat the CI space spanned by all the possible CSFs, the dimension of this CI space for VPA reaches about 4×10^5 . We need more than the half of all the solutions, but to obtain $O(10^5)$ solutions for all the ions is unrealistic. We therefore assumed additivity of the correlation energies, and use the $s^2 \rightarrow i'i''$ ($i'i'' = s's''$, $p'p''$, $d'd''$, and $f'f''$) CIs to perform NVPA and VPA CIs, after making tests to verify the validity of this assumption.

III. CALCULATIONS AND RESULTS

A. DFR TEs and spinor energies

We first discuss the characteristic features of several diagonal elements of the CI Hamiltonian, typically DFR TEs of the lowest state of the positive energies and the highest negative energies. These features have not previously been treated clearly.

The TEs and the highest and lowest spinor energies in DFR are collected in Table I. We denote the spinor with the highest and lowest spinor energies in the positive-energy states as $p80s$ and $p1s$, respectively, and the corresponding spinors in the negative-energy states as $n80s$ and $n1s$. In respective ions, the absolute value of the highest positive-spinor energy $\epsilon(p80s)$ and the lowest negative-spinor energy $\epsilon(n1s)$ are approximately equal. We recall the free electron Hamiltonian, giving the same two TEs except for the signs for the momentum p .

The $\epsilon(p80s)$ values are nearly equal for all the ions. We also find that the highest negative-spinor energy $\epsilon(p80s)$ value is approximately $-2c^2 = -37\,557.7$ hartrees for all the ions.

TABLE II. Kinetic energy, potential energy, and mass correction in DFR for He, Xe⁵²⁺, and Uuh¹¹⁴⁺ (in hartrees).

Lowest state in positive-energy states; $p1s^2$			
	He	Xe ⁵²⁺	Uuh ¹¹⁴⁺
TE	-2.861 813	-3002.946 288	-17 250.672 556
$\langle M \rangle$	-2.861 820	-3002.517 481	-17 045.536 906
$\langle T \rangle$	5.723 907	6267.390 770	47 199.656 970
$\langle V \rangle$	-5.723 900	-6267.819 577	-47 404.792 621
$\langle J \rangle^a$	1.025 834	35.634 590	108.669 068
Highest state in negative-energy states; $n80s^2$			
	He	Xe ⁵²⁺	Uuh ¹¹⁴⁺
TE	-75 115.598 117	-75 119.527 277	-75 124.214 737
$\langle M \rangle$	-75 115.441 068	-75 115.420 791	-75 115.418 143
$\langle T \rangle$	-0.017 213	-0.057 762	-0.063 050
$\langle V \rangle$	-0.139 837	-4.048 723	-8.733 544
$\langle J \rangle^b$	0.037 803	0.035 259	0.035 252

^a $J_{p1s,p1s}$.^b $J_{n80s,n80s}$.

The TEs of the lowest state of the positive energies and the highest state of the negative energies in DFR are given by the sum of the kinetic energy $\langle T \rangle$, potential energy $\langle V \rangle$, and the mass correction $\langle M \rangle$, which are shown in Table II,

$$\text{TE}(\text{DFR}) = \langle T \rangle + \langle V \rangle + \langle M \rangle. \quad (5)$$

For the lowest state in the positive-energy states, the virial theorem³⁰ shows that

$$\langle T \rangle + \langle V \rangle \approx 0. \quad (6)$$

The sum $\langle T \rangle + \langle V \rangle$ would be zero if the nucleus were a point charge. We see from Table II that this relation holds for ${}^2\text{He}$ to ${}_{116}\text{Uuh}$, and TE is close to $\langle M \rangle$.

For the highest state in the negative-energy state the relation (6) also holds. Recall that the kinetic energy is negative in the negative-energy states, so that $\langle T \rangle$ and $\langle V \rangle$ are both close to zero. That $\langle T \rangle \approx 0$ indicates that the highest spinor is almost wholly composed of small components, leading to $\text{TE} \approx -4c^2 = -75 115.4$ hartrees. The results in Table II support this claim. We also found that the electron-electron integrals $\langle J_{p1s,n80s} \rangle$ and $\langle K_{p1s,n80s} \rangle$ are less than 9 hartrees, and are small compared to c^2 , indicating that the spinor energy $\varepsilon(n80s) = \langle T \rangle / 2 + \langle V_n \rangle + 2\langle J_{p1s,n80s} \rangle - 2\langle K_{p1s,n80s} \rangle + \langle M \rangle / 2 \approx -37 557.7$ hartrees.

The Coulomb integral $J_{p1s,p1s}$ in the lowest positive-energy states increases as Z increases, indicating that $p1s$ contracts as Z increases, but $J_{n80s,n80s}$ in the highest negative-energy states is always around zero, indicating that $n80s$ spinors, which resemble each other, are very diffuse regardless of the nuclear charge. We may expect that any electron-electron repulsion terms including the highest negative-energy spinor are very small compared to $-2c^2$ as shown above, indicating that for any atoms the highest spinor energy in the negative-energy states is around $-2c^2$.

Dyall³¹ discussed the highest negative-energy spinors of $\text{Hg}^{78+} \sim \text{Hg}^{62+}$ in connection with the omission of the two-

electron integrals of the small component, where he gave that the ε 's are $-37 581.3 \sim -37 575.6$ hartrees and they are near to $-2c^2$.

Finally, using the results in Table I, we discuss the energy distribution of diagonal elements of the Hamiltonian matrix for the VPA. Values of $H'_{i,i}$ ($i=1,6400$) in the positive-energy states are in the ranges of $-2.9 \times 10^0 - 6.4 \times 10^8$, $-3.0 \times 10^3 - 6.4 \times 10^8$, and $-1.7 \times 10^4 - 6.4 \times 10^8$ for ${}^2\text{He}$, ${}^{54}\text{Xe}$, and ${}_{116}\text{Uuh}$, respectively. Values of $H'_{i,i}$ ($i=19201, 25600$) in the negative-energy states for these three ions have almost identical ranges of -7.5×10^4 to -6.4×10^8 . The $H_{i,i}$ values ($i=6401, 19200$), give the energy terms for virtual excitation of one electron in the positive- and the other electron in the negative-energy spinors. Values are between -3.2×10^8 and 3.2×10^8 for all ions, since these $H_{i,i}$'s are given approximately by the sum of the orbital energies $\varepsilon(p-ns) + \varepsilon(n-ns)$. Thus, any resulting "physical ground state of ions" and "physical low lying excited states" should be embedded in the virtual excitation terms.

B. Effect of removal of the no-virtual-pair approximation on $p1s^2 \rightarrow s's''$

We have performed two kinds of CI calculation, one of which includes CSFs spanned merely by both positive-energy spinors (NVPA), the other of which includes CSFs spanned by positive- and negative-energy spinors (VPA). Brown and Ravenhall¹³ pointed out that the instability could occur in many-electron systems if the negative-energy states are included. However, we found for $p1s^2 \rightarrow s's''$ CI that in almost all cases this inclusion causes no numerical problems.

We used 80 s -type primitive GTFs for the large component basis set, resulting in 80 p -type GTFs for the small component set. TEs, denoted by $\text{TE}(\text{DFR})$, $\text{TE}(\text{NVPA-CI}:s)$, and $\text{TE}(\text{VPA-CI}:s)$, are shown in Table III, where s indicates that $p1s^2 \rightarrow s's''$ CIs are considered; among the 25 600 VPA-CI solutions the solutions with $p1s^2$ character are found between 14 237 and 14 303; we disregard the solutions including the negative-energy states (spinors). It is ordinary thought that the inclusion of the negative-energy states brings the very low TEs because of the Brown and Ravenhall diseases, but Table III shows that $\text{TE}(\text{VPA-CI}:s)$ is energetically higher than $\text{TE}(\text{NVPA-CI}:s)$. The CI effects, namely, orthogonalizations to the lower solutions, lead for $\text{TE}(\text{VPA-CI}:s)$ to be higher than $\text{TE}(\text{NVPA-CI}:s)$. This gives that the absolute values of the correlation energy by the former, the $\text{CE}(\text{VPA}:s)$, are smaller than those of the latter, the $\text{CE}(\text{NVPA}:s)$. Resulting CEs in Fig. 1 confirm this discussion. We also see that the $\text{CE}(\text{NVPA}:s)$ depends more strongly on Z for larger nuclei than the $\text{CE}(\text{VPA}:s)$. At $Z=116$, the difference between the two CEs [hereafter $\delta\text{CE}(s)$] reaches 0.0096 hartrees, or 20% of the $\text{CE}(\text{NVPA}:s)$. Since the present basis set is almost complete, the results here give the limit of $\delta\text{CE}(s)$ with $p1s^2 \rightarrow s's''$ CIs. We strengthen here that, contrary to the common expectation, TE by VPA is always higher than that by NVPA.

TABLE III. Total energy by DFR and $p1s^2 \rightarrow s's''$ CI with NVPA and VPA (in hartrees).

Z	Mass	DFR	NVPA-CI: s	VPA-CI: s	Z	Mass	DFR	NVPA-CI: s	VPA-CI: s
2	4	-2.861 813	-2.879 164	-2.879 165	59	141	-3 619.248 642	-3 619.266 095	-3 619.265 339
3	7	-7.237 205	-7.253 287	-7.253 287	60	142	-3 750.519 155	-3 750.536 750	-3 750.535 938
4	9	-13.614 001	-13.629 570	-13.629 570	61	145	-3 884.526 414	-3 884.544 155	-3 884.543 302
5	11	-21.993 148	-22.008 440	-22.008 440	62	152	-4 021.297 867	-4 021.315 760	-4 021.314 862
6	12	-32.375 986	-32.391 108	-32.391 108	63	153	-4 160.886 845	-4 160.904 896	-4 160.903 951
7	14	-44.764 194	-44.779 203	-44.779 202	64	158	-4 303.307 609	-4 303.325 823	-4 303.324 830
8	16	-59.159 781	-59.174 709	-59.174 708	65	159	-4 448.614 604	-4 448.632 987	-4 448.631 944
9	19	-75.565 082	-75.579 952	-75.579 951	66	164	-4 596.825 128	-4 596.843 687	-4 596.842 591
10	20	-93.982 762	-93.997 590	-93.997 588	67	165	-4 747.999 837	-4 748.018 579	-4 748.017 429
11	23	-114.415 814	-114.430 611	-114.430 608	68	166	-4 902.168 618	-4 902.187 549	-4 902.186 343
12	24	-136.867 567	-136.882 341	-136.882 338	69	169	-5 059.365 820	-5 059.384 947	-5 059.383 683
13	27	-161.341 675	-161.356 435	-161.356 430	70	174	-5 219.632 834	-5 219.652 165	-5 219.650 842
14	28	-187.842 147	-187.856 897	-187.856 891	71	175	-5 383.038 835	-5 383.058 377	-5 383.056 982
15	31	-216.373 308	-216.388 053	-216.388 045	72	180	-5 549.596 468	-5 549.616 229	-5 549.614 785
16	32	-246.939 857	-246.954 602	-246.954 592	73	181	-5 719.391 021	-5 719.411 010	-5 719.409 473
17	35	-279.546 804	-279.561 553	-279.561 541	74	184	-5 892.443 862	-5 892.464 087	-5 892.462 487
18	40	-314.199 524	-314.214 279	-314.214 264	75	187	-6 068.816 756	-6 068.837 227	-6 068.835 556
19	39	-350.903 830	-350.918 595	-350.918 577	76	192	-6 248.550 399	-6 248.571 124	-6 248.569 378
20	40	-389.665 757	-389.680 535	-389.680 513	77	193	-6 431.741 612	-6 431.762 602	-6 431.760 779
21	45	-430.491 724	-430.506 517	-430.506 492	78	195	-6 618.416 486	-6 618.437 752	-6 618.435 847
22	48	-473.388 652	-473.403 464	-473.403 434	79	197	-6 808.642 844	-6 808.664 396	-6 808.662 408
23	51	-518.363 729	-518.378 562	-518.378 527	80	202	-7 002.455 715	-7 002.477 564	-7 002.475 490
24	52	-565.424 609	-565.439 465	-565.439 424	81	205	-7 199.965 449	-7 199.987 607	-7 199.985 444
25	55	-614.579 181	-614.594 063	-614.594 016	82	208	-7 401.223 255	-7 401.245 736	-7 401.243 487
26	56	-665.835 953	-665.850 863	-665.850 810	83	209	-7 606.325 106	-7 606.347 922	-7 606.345 531
27	59	-719.203 578	-719.218 519	-719.218 458	84	209	-7 815.338 896	-7 815.362 061	-7 815.359 589
28	58	-774.691 529	-774.706 504	-774.706 435	85	210	-8 028.317 348	-8 028.340 877	-8 028.338 302
29	63	-832.308 929	-832.323 940	-832.323 862	86	222	-8 245.180 542	-8 245.204 448	-8 245.201 763
30	64	-892.066 367	-892.081 416	-892.081 329	87	223	-8 466.345 401	-8 466.369 702	-8 466.366 899
31	69	-953.973 820	-953.988 909	-953.988 812	88	226	-8 691.704 533	-8 691.729 246	-8 691.726 301
32	74	-1018.042 459	-1018.057 591	-1018.057 484	89	227	-8 921.421 713	-8 921.446 856	-8 921.443 904
33	75	-1084.284 068	-1084.299 246	-1084.299 127	90	232	-9 155.471 890	-9 155.497 482	-9 155.494 359
34	80	-1152.709 760	-1152.724 986	-1152.724 855	91	231	-9 394.172 611	-9 394.198 673	-9 394.195 329
35	79	-1223.332 985	-1223.348 261	-1223.348 117	92	238	-9 637.301 107	-9 637.327 657	-9 637.324 223
36	84	-1296.165 127	-1296.180 457	-1296.180 299	93	237	-9 885.368 045	-9 885.395 109	-9 885.391 534
37	85	-1371.220 845	-1371.236 231	-1371.236 059	94	244	-10 138.052 555	-10 138.080 153	-10 138.076 429
38	88	-1448.513 123	-1448.528 567	-1448.528 379	95	243	-10 395.949 196	-10 395.977 356	-10 395.973 477
39	89	-1528.057 042	-1528.072 548	-1528.072 344	96	247	-10 658.777 592	-10 658.806 339	-10 658.802 300
40	90	-1609.867 216	-1609.882 788	-1609.882 566	97	247	-10 926.983 009	-10 927.012 374	-10 927.008 202
41	93	-1693.958 623	-1693.974 261	-1693.974 021	98	251	-11 200.397 788	-11 200.427 797	-11 200.423 384
42	98	-1780.347 158	-1780.362 867	-1780.362 608	99	252	-11 479.455 567	-11 479.486 255	-11 479.481 663
43	98	-1869.051 526	-1869.067 309	-1869.067 027	100	257	-11 763.984 091	-11 764.015 488	-11 764.010 704
44	102	-1960.086 284	-1960.102 143	-1960.101 841	101	258	-12 054.540 753	-12 054.572 899	-12 054.567 912
45	103	-2 053.471 656	-2 053.487 595	-2 053.487 271	102	259	-12 351.106 873	-12 351.139 806	-12 351.134 611
46	106	-2 149.224 342	-2 149.240 364	-2 149.240 017	103	262	-12 653.727 411	-12 653.761 170	-12 653.755 683
47	107	-2 247.365 236	-2 247.381 345	-2 247.380 973	104	261	-12 962.995 381	-12 963.030 015	-12 963.024 322
48	114	-2 347.910 197	-2 347.926 396	-2 347.925 998	105	262	-13 278.705 918	-13 278.741 473	-13 278.735 498
49	115	-2 450.885 987	-2 450.902 280	-2 450.901 856	106	266	-13 600.938 897	-13 600.975 418	-13 600.970 643
50	120	-2 556.308 409	-2 556.324 799	-2 556.324 346	107	264	-13 930.709 165	-13 930.746 715	-13 930.740 377
51	121	-2 664.204 540	-2 664.221 031	-2 664.220 549	108	269	-14 267.033 698	-14 267.072 322	-14 267.065 619
52	130	-2 774.588 584	-2 774.605 180	-2 774.604 668	109	268	-14 611.459 047	-14 611.498 819	-14 611.491 821
53	127	-2 887.499 699	-2 887.516 405	-2 887.515 860	110	271	-14 963.166 030	-14 963.207 007	-14 963.199 669
54	132	-3 002.946 288	-3 002.963 107	-3 002.962 530	111	272	-15 323.121 751	-15 323.164 009	-15 323.156 496
55	133	-3 120.964 196	-3 120.981 133	-3 120.980 521	112	285	-15 689.589 004	-15 689.632 585	-15 689.624 649
56	138	-3 241.571 633	-3 241.588 691	-3 241.588 044	113	284	-16 066.617 104	-16 066.662 127	-16 066.653 775
57	139	-3 364.804 634	-3 364.821 820	-3 364.821 135	114	289	-16 451.562 500	-16 451.609 033	-16 451.600 299
58	140	-3 490.687 227	-3 490.704 544	-3 490.703 821	115	288	-16 846.802 860	-16 846.851 020	-16 846.841 870
					116	292	-17 250.672 556	-17 250.722 424	-17 250.712 840

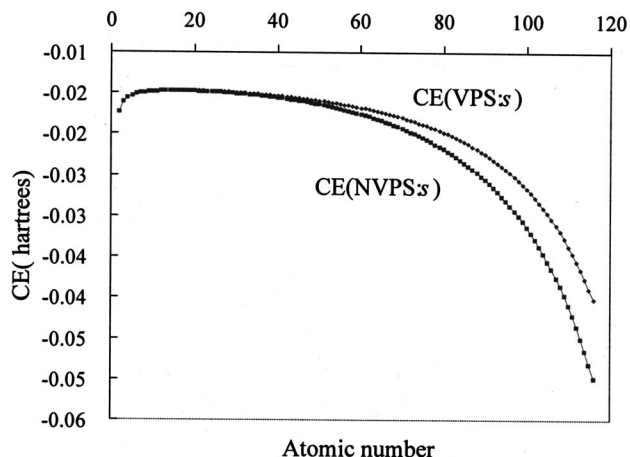


FIG. 1. Correlation energies calculated with (VPA) and without virtual-pair approximation (NVPA) using s -type pGTFs as large component basis set, in hartrees.

C. Effect of removal of the no-virtual-pair approximation on $p1s^2 \rightarrow i'i''$

The effect of the removal of NVPA for heavier atoms is larger than expected. To show the effect of the higher angular momentum spinors, we discuss the results of VPA calculations using p , d , and f spinors together with s spinors in the present subsection. The correlation energy contributions were calculated under the assumption of additivity. The truncations of the basis set are also detailed in this subsection. Effects of the assumption of additivity and the truncations of the basis set are very small as shown below.

Let us discuss how to evaluate $\delta CE(i)$. Use of the full basis set is difficult because of the large number of spinors. Present CI program treats distinctively the two strings of subspecies from time reversal symmetry, and used only the CSFs with the total angular momentum=0. If we use 80 pGTFs for the s , p , d , and f subsymmetries, the numbers of spinors for the respective subspecies are 160, 480, 800, and 1120. We therefore selected the pGTFs for the CI calculations. We used the DFR results; pGTFs having coefficient greater than 0.01 in DFR $p1s$ were selected (the exponent parameters for these pGTFs are applied to p -, d -, and f -pGTFs for the correlation calculations). The numbers of the pGTFs for the respective symmetries are the same, and are 12–18 depending on the ions under consideration.

The total numbers of the selected pGTFs are 400–600 under the subsymmetries. It is preferable to treat the CI space spanned with all the possible CSFs, but the dimension of this CI space for the VPA reaches 4×10^5 . The physically proper solutions are embedded in the virtual excited solutions in the VPA case, and we do not know where it is. Then to obtain physically proper solutions we need to solve all the solutions; thus the smaller CI matrices were required. We assume (1) additivity of the correlation energy, $CE = CE(s) + CE(p) + CE(d) + CE(f)$, where $CE(i)$ is obtained from the CI including $p1s^2 \rightarrow i'i''$ ($i'i'' = s's'', \dots, f'f''$) and (2) the additivity in δCE ,

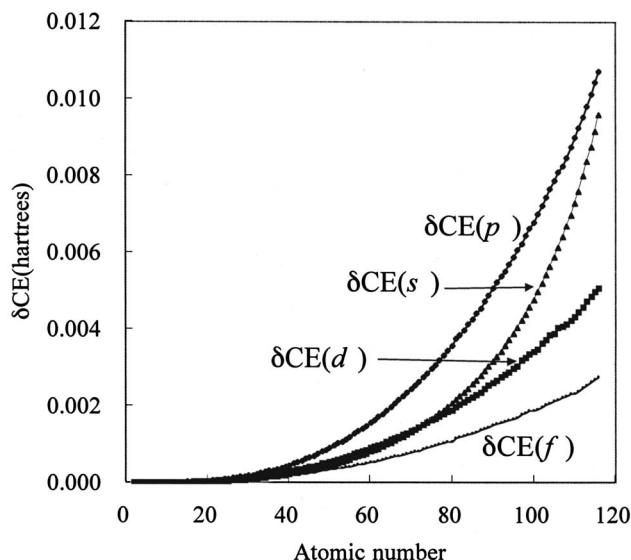


FIG. 2. Partial correlation corrections of $\delta CE(s)$, $\delta CE(p)$, $\delta CE(d)$, and $\delta CE(f)$ arising from VPA in hartrees.

$$\delta CE = \delta CE(s) + \delta CE(p) + \delta CE(d) + \delta CE(f), \quad (7)$$

$$\delta CE(i) = CE(VPA:i) - CE(NVPA:i).$$

Then the $CE(VPA)$ is calculated as the sum of the $CE(NVPA)$ and δCE ,

$$CE(VPA) \approx CE(NVPA) + \delta CE. \quad (8)$$

1. On $\delta CE(s)$: Truncation of basis set

The δCE calculated from the s -full CI, denoted as $\delta CE(\text{full-CI}:s)$, moves from 0.000 00 to 0.009 583 hartrees as Z increases from 2 to 116. The δCE value calculated from selected pGTFs [denoted as $\delta CE(\text{selected-CI}:s)$] increases from 0.000 00 to 0.009 621 hartrees. Curves of $\delta CE(\text{full-CI}:s)$ and $\delta CE(\text{selected-CI}:s)$ versus nuclear charge Z are very similar. The maximum difference between two δCE s is 0.000 068 hartrees at $Z=89$, which is $\sim 1/40$ of $\delta CE(\text{full-CI}:s)$: 0.002 953 and $\delta CE(\text{selected-CI}:s)$: 0.003 019 hartrees. We can therefore safely use this $\delta CE(\text{selected-CI}:s)$ as $\delta CE(s)$. Figure 2 shows $\delta CE(s)$ calculated from selected-CI, increasing monotonically as the atomic number increases. This indicates that the VPA causes the absolute value of the correlation energy to be less than those of NVPA for heavier ions.

2. On $\delta CE(p)$

We have tested two kinds of CI calculations: one uses the configurations $(s's'' + p'p'')$ and the other uses a single configuration for $s's''$, namely, two electrons in $p1s$ plus $p'p''$, abbreviated as $(p1s^2 + p'p'')$. The two CEs and two $\delta CE(p)$'s are given by

TABLE IV. CE(Hylleraas) (see Refs. 5 and 6) CE(VPA:*spdf*), and CE(NVPA:*spdf*) in hartrees.

Z	Hylleraas	CE(NVPA)	CE(VPA)	Z	Hylleraas	CE(NVPA)	CE(VPA)
2	-0.042 044	-0.041 644	-0.041 644	59	-0.044 915	-0.047 410	-0.043 808
3	-0.043 495	-0.042 965	-0.042 965	60	-0.044 893	-0.047 548	-0.043 777
4	-0.044 259	-0.043 645	-0.043 644	61	-0.044 872	-0.047 693	-0.043 748
5	-0.044 723	-0.044 060	-0.044 060	62	-0.044 854	-0.047 843	-0.043 715
6	-0.045 032	-0.044 339	-0.044 338	63	-0.044 839	-0.048 001	-0.043 690
7	-0.045 250	-0.044 538	-0.044 536	64	-0.044 825	-0.048 197	-0.043 623
8	-0.045 412	-0.044 687	-0.044 683	65	-0.044 815	-0.048 372	-0.043 598
9	-0.045 534	-0.044 789	-0.044 783	66	-0.044 808	-0.048 554	-0.043 576
10	-0.045 629	-0.044 883	-0.044 873	67	-0.044 804	-0.048 744	-0.043 556
11	-0.045 703	-0.044 959	-0.044 945	68	-0.044 803	-0.048 942	-0.043 539
12	-0.045 762	-0.045 008	-0.044 989	69	-0.044 806	-0.049 149	-0.043 526
13	-0.045 808	-0.045 047	-0.045 023	70	-0.044 814	-0.049 364	-0.043 516
14	-0.045 844	-0.045 096	-0.045 062	71	-0.044 825	-0.049 589	-0.043 510
15	-0.045 872	-0.045 121	-0.045 078	72	-0.044 841	-0.049 823	-0.043 508
16	-0.045 894	-0.045 142	-0.045 089	73	-0.044 863	-0.050 106	-0.043 459
17	-0.045 909	-0.045 178	-0.045 109	74	-0.044 889	-0.050 364	-0.043 463
18	-0.045 919	-0.045 193	-0.045 110	75	-0.044 922	-0.050 633	-0.043 472
19	-0.045 925	-0.045 206	-0.045 108	76	-0.044 960	-0.050 912	-0.043 486
20	-0.045 927	-0.045 235	-0.045 112	77	-0.045 005	-0.051 204	-0.043 483
21	-0.045 925	-0.045 248	-0.045 105	78	-0.045 057	-0.051 508	-0.043 507
22	-0.045 921	-0.045 258	-0.045 093	79	-0.045 117	-0.051 824	-0.043 535
23	-0.045 913	-0.045 269	-0.045 079	80	-0.045 184	-0.052 153	-0.043 582
24	-0.045 903	-0.045 297	-0.045 069	81	-0.045 260	-0.052 541	-0.043 517
25	-0.045 890	-0.045 310	-0.045 052	82	-0.045 345	-0.052 902	-0.043 592
26	-0.045 875	-0.045 322	-0.045 031	83	-0.045 440	-0.053 280	-0.043 644
27	-0.045 859	-0.045 336	-0.045 009	84	-0.045 545	-0.053 674	-0.043 704
28	-0.045 840	-0.045 350	-0.044 986	85	-0.045 661	-0.054 085	-0.043 772
29	-0.045 820	-0.045 384	-0.044 962	86	-0.045 789	-0.054 512	-0.043 847
30	-0.045 798	-0.045 403	-0.044 936	87	-0.045 929	-0.054 959	-0.043 934
31	-0.045 774	-0.045 424	-0.044 908	88	-0.046 083	-0.055 470	-0.043 982
32	-0.045 749	-0.045 444	-0.044 878	89	-0.046 252	-0.055 962	-0.044 085
33	-0.045 723	-0.045 468	-0.044 847	90	-0.046 435	-0.056 474	-0.044 202
34	-0.045 696	-0.045 493	-0.044 816	91	-0.046 635	-0.057 011	-0.044 333
35	-0.045 667	-0.045 542	-0.044 778	92	-0.046 853	-0.057 570	-0.044 483
36	-0.045 638	-0.045 574	-0.044 744	93	-0.047 089	-0.058 157	-0.044 683
37	-0.045 608	-0.045 608	-0.044 710	94	-0.047 346	-0.058 766	-0.044 878
38	-0.045 577	-0.045 644	-0.044 674	95	-0.047 624	-0.059 408	-0.045 068
39	-0.045 545	-0.045 683	-0.044 638	96	-0.047 926	-0.060 078	-0.045 267
40	-0.045 513	-0.045 726	-0.044 602	97	-0.048 252	-0.060 840	-0.045 436
41	-0.045 480	-0.045 793	-0.044 551	98	-0.048 606	-0.061 580	-0.045 694
42	-0.045 447	-0.045 844	-0.044 513	99	-0.048 989	-0.062 358	-0.045 957
43	-0.045 413	-0.045 898	-0.044 474	100	-0.049 402	-0.063 172	-0.046 332
44	-0.045 379	-0.045 955	-0.044 436	101	-0.049 848	-0.064 029	-0.046 683
45	-0.045 345	-0.046 016	-0.044 397	102	-0.050 331	-0.064 983	-0.047 017
46	-0.045 311	-0.046 080	-0.044 357	103	-0.050 854	-0.065 933	-0.047 403
47	-0.045 277	-0.046 148	-0.044 319	104	-0.051 419	-0.066 937	-0.047 813
48	-0.045 243	-0.046 245	-0.044 256	105	-0.052 029	-0.067 991	-0.048 266
49	-0.045 209	-0.046 324	-0.044 211	106	-0.052 691	-0.069 096	-0.048 724
50	-0.045 176	-0.046 407	-0.044 174	107	-0.053 405	-0.070 271	-0.049 230
51	-0.045 143	-0.046 495	-0.044 135	108	-0.054 178	-0.071 498	-0.049 811
52	-0.045 111	-0.046 587	-0.044 097	109	-0.055 017	-0.072 804	-0.050 432
53	-0.045 080	-0.046 684	-0.044 059	110	-0.055 924	-0.074 173	-0.051 117
54	-0.045 049	-0.046 785	-0.044 022	111	-0.056 909	-0.075 626	-0.051 840
55	-0.045 020	-0.046 892	-0.043 986	112	-0.057 977	-0.077 217	-0.052 552
56	-0.044 991	-0.047 032	-0.043 911	113	-0.059 137	-0.078 914	-0.053 359
57	-0.044 964	-0.047 152	-0.043 876	114	-0.060 399	-0.080 635	-0.054 214
58	-0.044 939	-0.047 278	-0.043 841	115	-0.061 773	-0.082 483	-0.055 185
				116	-0.063 270	-0.084 423	-0.056 187

$$\begin{aligned}
CE(I:p) &= TE(I:s's'' + p'p'') - TE(I:s's''), \\
CE'(I:p) &= TE(I:p1s^2 + p'p'') - TE(I:p1s^2), \\
\delta CE(p) &= CE(VPA:p) - CE(NVPA:p), \\
\delta CE'(p) &= CE'(VPA:p) - CE'(NVPA:p), \\
I &= NVPA \text{ or } VPA.
\end{aligned} \tag{9}$$

Calculated $\delta CE(p)$'s for $Z=2-116$ lie between 0.000 000 and 0.010 712, and $\delta CE'(p)$ values are 0.000 000–0.010 635 hartrees. The maximum difference between $\delta CE(p)$ and $\delta CE'(p)$ is 0.000 117 at $Z=107$ where $\delta CE(p)$ is 0.008 228 and $\delta CE'(p)$ is 0.008 345 hartrees. Curves of $\delta CE(p)$ and $\delta CE'(p)$ versus nuclear charge are very similar. Since $\delta CE'(p) = \delta CE(p)$, we could use $\delta CE'(p)$ instead of $\delta CE(p)$ to an accuracy of 0.0001 hartrees. Figure 2 shows $\delta CE(p)$ using $p1s^2 + p'p''$. The $\delta CE(p)$ value is positive and larger than $\delta CE(s)$; VPA reduces the absolute value of CE considerably compared to $\delta CE(s)$. From the discussion on $\delta CE(p)$ and $\delta CE'(p)$, we expect $\delta CE'(i) = \delta CE(i)$ with $i \geq d$ and hereafter use $\delta CE'(i)$ instead of $\delta CE(i)$.

3. On $\delta CE(d)$ and $\delta CE(f)$

We have evaluated $\delta CE(d)$ and $\delta CE(f)$ using the configurations $(p1s^2 + d'd'')$ and $(p1s^2 + f'f'')$. The resulting $\delta CE(d)$ and $\delta CE(f)$ are shown in Fig. 2. They are positive, raising the CE(VPA) relative to the CE(NVPA).

The CE calculated from Eq. (8), denoted by the CE(VPA:*spdf*), is given in Table IV and in Fig. 3 together with values of the CE(NVPA:*spdf*) and CE(Hylleraas). We see that the VPA reduces the absolute value of the CE, and that the CE(VPA:*spdf*) mimics CE(Hylleraas).

The CE(NVPA:*spdf*) exceeds CE(Hylleraas) for ions $\geq_{38}\text{Sr}$, as shown in Fig. 3. The DF calculation with Hylleraas-type functions is not possible. We cannot therefore set the positive-energy Hylleraas-type CSFs apart from the negative-energy ones, a step which indicates that the Hylleraas-type CI includes contributions from the negative-energy states. The agreement of CE(Hylleraas) and the CE(VPA:*spdf*) indicates that differences between CE(Hylleraas) and the CE(NVPA:*spdf*) arise from implicit inclusion of the virtual-pair excitations in the Hylleraas-CI. Although the NVPA brings the greater changes, we emphasize that the sharp fall in the CEs for heavier ions are not an artifact but an essential effect of relativity.

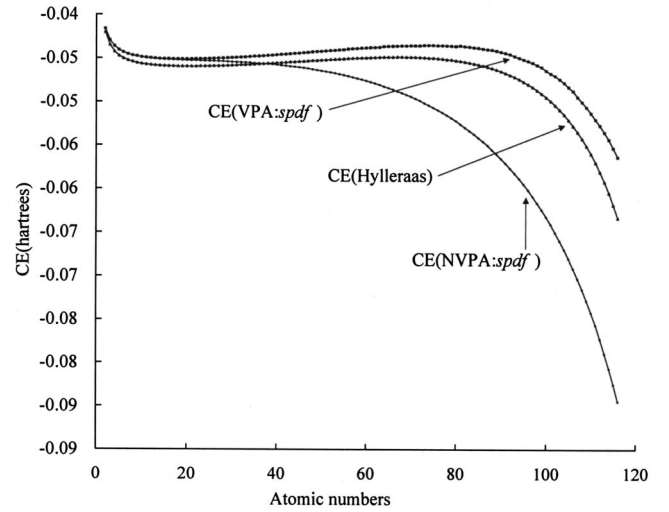


FIG. 3. Correlation energies, CE(NVPA:*spdf*), CE(VPA:*spdf*), and CE(Hylleraas) in hartrees.

We comment here on the small maximum in CE(Hylleraas) and the CE(VPA:*spdf*) in Fig. 3. We know that in DFR or NDF the electrons occupy the large and small components. By comparing this with the numbers in the nonrelativistic Hartree-Fock wave function, equal to 2, we infer that the electrons in the four component DF wave functions are polarized since the small components have a p character and are much more localized near the nucleus; we called this “relativistic precorrelation” in the previous work³² where precorrelation was defined by Clementi for the nonrelativistic Hartree-Fock wave functions with parallel spins.¹ As discussed,³² the electrons in the small component increase in number as the nuclear charge increases. Thus the relativistic polarization in DFR increases as the nuclear charge increases, reducing $|CE(\text{rel})|$. On the other hand, an increase in the nuclear charge causes the charge cloud to contract, leading to stronger electron-electron interaction and raising $|CE(\text{rel})|$. Two opposing trends give rise to the maximum in $|CE(\text{rel})|$ at $_{68}\text{Er}$.

We now compare our results with previous ones. Using $p1s^2 \rightarrow s's''$, Jáuregui *et al.*²⁵ discussed TE with the VPA for U^{+90} but did not give $\delta CE(s)$. Sapirstein *et al.*¹⁹ gave $\delta CE(s)$, $\delta CE(p)$, and $\delta CE(d)$ for U^{+90} , which are 0.0034, 0.0055, and 0.0028 hartrees, compared to the present values of 0.0031, 0.0050, and 0.0026 hartrees. Using the S -matrix method, Lindgren *et al.*²⁴ evaluated the correction $\delta CE(S\text{-matrix})$ arising from VPA for the He-like ions with Z

TABLE V. Approximate correlations energies CE(NVPA:*spdf*), CE(VPA:*spdf*), and δCE calculated with the assumption of additivity under the uniform and point charge nucleus models in hartrees.

	CE(NVPA: <i>spdf</i>)		CE(VPA: <i>spdf</i>)		δCE	
	uniform	point	uniform	point	uniform	point
Hg ⁷⁸⁺	−0.0522	−0.0523	−0.0436	−0.0436	0.0086	0.0087
Th ⁸⁸⁺	−0.0565	−0.0567	−0.0442	−0.0444	0.0123	0.0123
Fm ⁹⁸⁺	−0.0632	−0.0638	−0.0463	−0.0467	0.0168	0.0171
Ds ¹⁰⁸⁺	−0.0742	−0.0763	−0.0511	−0.0524	0.0231	0.0240

$=2, 4, 6, \dots, 80$, and 92, where $\delta\text{CE}(S\text{-matrix})$ gives all the contributions from the partial waves of $s, p, d, \dots, \infty$. Their correction δCE values are slightly smaller than ours. For example, $\delta\text{CE}(S\text{-matrix})$ for U^{90+} is 0.0109 hartrees, whereas the present δCE defined by Eq. (7) is 0.0122 hartrees.

We here add the very recent Hylleraas-type calculation performed by Pestka *et al.*:³³ CEs for Hg^{78+} and Th^{88+} given by them are -0.0431 and -0.0443 hartrees while corresponding values [the $\text{CE}(\text{VPA}:spdf)$] in Table IV are -0.0436 and -0.0442 hartrees.

We now see the dependence of CE on the nucleus model. We have calculated the approximate correlation energies for Hg^{78+} , Th^{88+} , Fm^{98+} , and Ds^{108+} with the uniform and point charge models under the additivity of CEs discussed in this subsection. The results are given in Table V. We see quite a similarity between the two CEs: we can use both models to discuss the correlation energies of the He isoelectronic sequence. Slight differences in CEs between Tables IV and V come from the fact that the former does not assume the additivity of CEs.

The present calculation shows the importance of taking account of the VPA in obtaining proper electronic correlations for inner shell electrons of systems including heavier atoms. It is necessary to take account of the VPA when considering electronic correlations between the inner shell and outer shell electrons of these systems so far as we consider the Dirac-Coulomb Hamiltonian.

IV. CONCLUSION

We have investigated correlation energies (CEs) in He-like ions with and without the virtual-pair approximation: the two CEs are denoted as the $\text{CE}(\text{VPA})$ and the $\text{CE}(\text{NVPA})$. Hereafter we denote the lowest state in the positive-energy state in DFR as $p1s^2$. We performed a full CI calculation including only $p1s^2 \rightarrow s's''$ excitations, where the set used was a universal set and the large components were spanned with 80 primitive s -like Gaussian-type functions. We applied this to ${}_2\text{He}$ through ${}_{116}\text{Uuh}^{114+}$. We found that CI with VPA does not cause Brown and Ravenhall diseases and moreover CI total energies for the positive-state with VPA are always higher than those with NVPA. Following this, we found that the $\text{CE}(\text{VPA}:s)$ is in the range from -0.014734 to -0.040274 hartrees, while that the $\text{CE}(\text{NVPA}:s)$ is from -0.014744 to -0.049865 hartrees, where the $\text{CE}(\text{VPA}:s)$ denotes the correlation energy given by VPA CI with $p1s^2 \rightarrow s's''$ excitations; a similar notation is used for NVPA calculation. $|\text{CE}(\text{VPA}:s)|$ is much smaller than $|\text{CE}(\text{NVPA}:s)|$ for heavier atoms. The effect of the inclusion of the virtual-pairs exceeds what we expected. We evaluated the correction δCE arising from the VPA, assuming that this is expressed as the sum of the partial correlation corrections from $p1s^2 \rightarrow s's''$, $p1s^2 \rightarrow p'p''$, $p1s^2 \rightarrow d'd''$, and $p1s^2 \rightarrow f'f''$ CIs. Using this δCE , we modified previous values of the $\text{CE}(\text{NVPA}:spdf)$ (Ref. 12) and obtained the $\text{CE}(\text{VPA}:spdf)$ as $\text{CE}(\text{NVPA}:spdf) + \delta\text{CE}$. The correction δCE was consid-

erable. The $\text{CE}(\text{VPA}:spdf)$ values agree with $\text{CE}(\text{Hylleraas})$'s,^{5,6,32} indicating that it is essential to consider excitations into negative-energy states, for systems including heavier ions under the Dirac-Coulomb Hamiltonian. It may be required to include the effects from the negative sea which is disregarded in the present work.

We finally comment that the sharp CE fall found firstly by Pestka and Karwowski for heavier He-like ions^{5,6} is not an artifact of the calculation but is an essential consequence of the relativity.

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