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Commentationes

Perturbation Calculations on the Split-Shell Wavefunctions of Two-Electron Atoms

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In a special case of the Löwdin-Adams variant of perturbation theory, knowledge of the perturbed wavefunction through first order is sufficient for the calculation of the energy correct to the fifth order. This is applied to the split-shell wavefunctions of H^-, He, and Li^+. The results are presented, compared with other approaches, and discussed.

Key words: Helium isoelectronic series – Split-shell wavefunctions – Löwdin-Adams perturbation theory – Off-diagonal perturbation – Scaled perturbation

1. Introduction

In the course of our recent studies [1] on the distinguishable electron method (DEM), we came to realize that it would be desirable to perform non-DEM perturbation calculations on the split-shell $1s1s'$ wavefunction

$$\Phi = C[\exp(-\alpha r_1 - \beta r_2) + \exp(-\beta r_1 - \alpha r_2)] \tag{1}$$

for helium-like atoms. This problem was used by Lebeda and Schrader [2] as a test case for their method of perturbation calculations without H^0 or H^1. In their method, the existence of a Sternheimer potential is implicitly assumed, but one does not need to obtain that potential explicitly. In their calculation, Lebeda and Schrader solved for the first-order wavefunction Ψ^1 by a variational expansion in the basis set $\{\Phi s^I t^J u^K\}$, where s, t, and u are the familiar coordinates $r_1 + r_2$, $r_1 - r_2$, and r_{12} respectively, and $\max(I + J + K) = 4$.

In the present study, on the other hand, we apply the perturbation formalism developed by Löwdin [3] and Adams [4] and solve for Ψ^1 by variational expansion in the same kind of basis set that was used by Lebeda and Schrader [2]. The results will be compared with theirs as well as other approaches.

2. Calculation and Results

2.1. Löwdin-Adams Perturbation Theory[1]

In the Löwdin-Adams variant [3, 4] of nondegenerate perturbation theory, the total Hamiltonian operator $\mathscr{H}$ is partitioned by projection operators $\mathscr{O}$ and

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[1] See also the recent paper by Devine and Stewart [5].

$\mathscr{P}(=\mathscr{I}-\mathscr{O})$ into an unperturbed part

$$\mathscr{h}=\mathscr{O}\mathscr{H}\mathscr{O}+\mathscr{P}\mathscr{H}\mathscr{P} \tag{2}$$

and a perturbing potential

$$\mathscr{V}=\mathscr{H}-\mathscr{h}=\mathscr{P}\mathscr{H}\mathscr{O}+\mathscr{O}\mathscr{H}\mathscr{P}\,. \tag{3}$$

The operator $\mathscr{O}$ is the projection operator onto the subspace spanned by N linearly independent basis functions x_k

$$\mathscr{O}=\sum_k^N\sum_l^N|x_k\rangle W_{kl}\langle x_l|\,, \tag{4}$$

$$\boldsymbol{W}=\boldsymbol{S}^{-1}\,, \tag{5}$$

$$S_{kl}=\langle x_k|x_l\rangle\,. \tag{6}$$

Using the projection operator property of $\mathscr{O}$ and $\mathscr{P}$, Adams proved [4] that, for any non-negative integer n,

$$E^{2n+1}=0\,, \tag{7}$$

$$\mathscr{O}\,\Psi^{2n+1}=0=\mathscr{P}\,\Psi^{2n}\,, \tag{8}$$

and analyzed [4] the perturbation corrections to configuration-interaction wavefunctions constructed within the subspace defined by $\mathscr{O}$. On the other hand, we are primarily interested in the special case of $N=1$, and shall only make use of Adams' result that E^1, E^3, E^5, $\mathscr{O}\,\Psi^1$, and $\mathscr{P}\,\Psi^2$ are all equal to zero.

2.2. *Special Case: N = 1*

Let us apply the usual Rayleigh-Schrödinger perturbation theory [6] to our $\mathscr{H}=\mathscr{h}+\mathscr{V}$, as defined in (2) and (3), for the case of $N=1$. With the definitions

$$\Phi=\Psi^0=x_1\,, \tag{9}$$

$$\langle\Phi|\Phi\rangle=1\,, \tag{10}$$

one can readily derive

$$E^0=\langle\Phi|\mathscr{H}|\Phi\rangle\,, \tag{11}$$

$$\mathscr{P}\,[(\mathscr{H}-E^0)\,\Psi^1+\mathscr{H}\,\Phi]=0\,, \tag{12}$$

$$E^2=\langle\Phi|\mathscr{H}|\Psi^1\rangle\,. \tag{13}$$

Moreover, because $N=1$ and $\mathscr{P}\,\Psi^2=0$,

$$\Psi^2=-\Phi\langle\Psi^1|\Psi^1\rangle/2\,, \tag{14}$$

$$E^4=-\langle\Psi^1|\Psi^1\rangle E^2\,. \tag{15}$$

It appears that, in this special case, we can compute the energy correct to $\mathrm{O}(\lambda^5)$, given the wavefunction correct to $\mathrm{O}(\lambda)$. However, since (12) cannot be solved exactly, we seek a variational solution. The second-order energy functional for our problem is [5].

$$\tilde{E}^2 = \langle \Phi | \mathscr{H} | \psi \rangle + \langle \psi | \mathscr{H} | \Phi \rangle + \langle \psi | \mathscr{H} | \psi \rangle - E^0 \langle \psi | \psi \rangle \tag{16}$$

where $\mathscr{P}\psi = \psi = \tilde{\Psi}^1$. As $E^2 \leqq \tilde{E}^2$ for ground states, ψ is varied to minimize $\tilde{E}^2$. After the optimization, we can estimate Ψ^2 and E^4 with (14) and (15) respectively.

2.3. Computational Procedure

For the unperturbed wavefunctions Φ in Eq. (1), we take the more recent parameters obtained by ten Hoor [7] instead of the older values [8].

Next, we construct the basis set $\{\Phi s^I t^J u^K\}$ with $\max(I+J+K)=5$, and transform by a Schmid orthonormalization to the set $\{\eta\}$ with $\eta_1 = \Phi$. Then, the Hamiltonian matrix $\boldsymbol{H}$ for this basis set excluding η_1 is diagonalized. The resulting eigenvectors $\{\varphi\}$ are used in the variational solution of ψ in the usual manner [6]: Let

$$\psi = \sum_k \varphi_k a_k \tag{17}$$

where

$$\langle \varphi_k | \mathscr{H} | \varphi_l \rangle = \delta_{kl} \varepsilon_l \,. \tag{18}$$

Then, Eq. (16) becomes

$$\tilde{E}^2 = \sum_k \{ \langle \Phi | \mathscr{H} | \varphi_k \rangle a_k + a_k^* \langle \varphi_k | \mathscr{H} | \Phi \rangle + a_k^* (\varepsilon_k - E^0) a_k \} \,. \tag{19}$$

Therefore, $\tilde{E}^2$ becomes a minimum

$$\tilde{E}^2 = \sum_k \langle \Phi | \mathscr{H} | \varphi_k \rangle a_k \tag{20}$$

when

$$a_k = (E^0 - \varepsilon_k)^{-1} \langle \varphi_k | \mathscr{H} | \Phi \rangle \,. \tag{21}$$

Finally, from (15),

$$\tilde{E}^4 = -A\tilde{E}^2 \tag{22}$$

where

$$A = \sum_k a_k^* a_k \,. \tag{23}$$

2.4. Results

Numerical results of our perturbation calculations are presented in Table 1 for the ground states of H^-, He, and Li^+. The partial sums $E(L)$ and the energy expectation values are defined as

$$E(L) = \sum_{l=0}^{L} E^l \,, \tag{24}$$

$$\mathscr{E}(L) = \langle \Psi(L) | \mathscr{H} | \Psi(L) \rangle / \langle \Psi(L) | \Psi(L) \rangle \,, \tag{25}$$

Table 1. Results of perturbation calculations (in atomic units)

	$Z=1$	$Z=2$	$Z=3$
$E(0)=E(1)$	-0.51330289	-2.8756613	-7.2487479
$E(2)=E(3)$	-0.52763274	-2.9037819	-7.2799218
$E(4)=E(5)$	-0.52682354	-2.9036320	-7.2798509
$\mathscr{E}(1)=\mathscr{E}_a$	-0.52686680	-2.9036328	-7.2798511
$\mathscr{E}(2)=\mathscr{E}_b$	-0.52681277	-2.9036318	-7.2798509
$\mathscr{E}_c$	-0.52690378	-2.9036336	-7.2798512
E_{CI}	-0.52704774	-2.9036344	-7.2798514
E_{exact} [a]	-0.52775102	-2.9037244	-7.2799134

[a] Ref. [9].

Table 2. Dependence of results on M [a]

	M	$Z=1$	$Z=2$	$Z=3$
A	1	0.01161980	0.00481505	0.00222470
	2	0.04603719	0.00533377	0.00223462
	3	0.04910319	0.00507333	0.00224084
	4	0.05332882	0.00532828	0.00227756
	5	0.05646904	0.00533052	0.00227268
$-E^2$	1	0.00645260	0.02026903	0.02348409
	2	0.01126567	0.02725800	0.03035494
	3	0.01328360	0.02768598	0.03085151
	4	0.01398963	0.02799695	0.03109234
	5	0.01432985	0.02812055	0.03117390
$-E_{\mathrm{CI}}$	1	0.51968340	2.8958338	7.2721800
	2	0.52418342	2.9027760	7.2790353
	3	0.52608698	2.9032090	7.2795307
	4	0.52674662	2.9035115	7.2797698
	5	0.52704774	2.9036344	7.2798514

[a] Defined as $\max(I+J+K)$ for the basis set $\{\Phi\, s^I t^J u^K\}$.

where

$$\Psi(L) = \sum_{l=0}^{L} \Psi^l \tag{26}$$

and the tildes are suppressed for simplicity[2]. The scaled energies $\mathscr{E}_\mu$ with $\mu = a$, b, and c, will be discussed in Section 2.5. Also included in Table 1 are E_{CI} and E_{exact} [9], the former being the result of configuration-interaction (CI) calculations within the given basis set.

Comparison of $E(3)$ with $\mathscr{E}(1)$, and $E(5)$ with $\mathscr{E}(2)$ and with E_{CI} indicates fairly rapid convergence of our perturbation series. On the other hand, the rate of convergence with respect to basis size is somewhat inferior: The difference $E_{\mathrm{CI}} - E_{\mathrm{exact}}$ and the convergence data shown in Table 2 are both indications of the incompleteness of our basis.

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[2] It is to be understood that errors are present as a result of the finite expansion in Eq. (17).

Table 3. Comparison of errors in $E(L)$: (a) Z^{-1} expansion of Scherr and Knight [10], (b) ζ^{-1} expansion of Sanders and Hirschfelder [11], (c) $1s1s'$ calculated by Lebeda and Schrader [2], and (d) $1s1s'$ calculated in this work

	L	$Z=1$	$Z=2$	$Z=3$
(a)	0	−0.472249	−1.096276	−1.720087
	1	0.152751	0.153724	0.154913
	2	−0.004915	−0.003942	−0.002753
	3	0.003784	0.000407	0.000147
	4	0.002895	0.000185	0.000048
	5	0.001859	0.000056	0.000010
(b)	0	0.055095	0.056068	0.057257
	1	0.055095	0.056068	0.057257
	2	−0.004915	−0.003942	−0.002753
	3	0.007738	0.001213	0.000484
	4	0.000106	−0.000054	−0.000016
	5	0.001240	0.000023	0.000003
(c)	0	0.014448	0.028063	0.031166
	1	0.014448	0.028063	0.031166
	2	−0.00129	−0.00321	−0.00235
	3	0.00339	0.00072	0.00038
(d)	0	0.014448	0.028063	0.031166
	1	0.014448	0.028063	0.031166
	2	0.000118	−0.000058	−0.000008
	3	0.000118	−0.000058	−0.000008
	4	0.000927	0.000092	0.000062
	5	0.000927	0.000092	0.000062

In Table 3, we compare the errors in $E(L)$ from our calculation with those for the familiar Z^{-1} expansion of Scherr and Knight [10], the ζ^{-1} expansion of Sanders and Hirschfelder [11], and the split-shell calculation of Lebeda and Schrader [2]. It can be seen that our $E(2)=E(3)$ are better than those of the other approaches[3]. On the other hand, E^4 in this work tends to over-correct $E(3)$ and to make $E(4)=E(5)$ too high. This can be understood in terms of the analysis given below.

2.5. *Scaled Perturbation Theory*[4]

Table 1 shows that $\mathscr{E}(1)<\mathscr{E}(2)$ for the examples considered. This implies that Ψ^2 overcorrects $\Psi(1)$, which can be seen from another angle: If one defines

$$\Psi_\mu=\Phi+\mu\Psi^1\,, \tag{27}$$

$$\mathscr{E}_\mu=\langle\Psi_\mu|\mathscr{H}|\Psi_\mu\rangle/\langle\Psi_\mu|\Psi_\mu\rangle\,, \tag{28}$$

then, for our special case[5],

$$\mathscr{E}_\mu=E^0+E^2\mu(2-\mu)/(1+\mu^2A)\,. \tag{29}$$

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[3] This is true even when we use E^2 for $M=4$ from Table 2 (to be fair to Lebeda and Schrader).

[4] See Refs. [12–14] and references therein for scaled perturbation theory.

[5] In general [13],

$$\mathscr{E}_\mu=E^0+E^1+[\mu(2-\mu)E^2+\mu^2E^3]/(1+\mu^2A)\,.$$

It can be seen that

$$\mathscr{E}(1)=\mathscr{E}_a, \quad a=1\,, \tag{30}$$

$$\mathscr{E}(2)=\mathscr{E}_b, \quad b=(1-A/2)^{-1}\,, \tag{31}$$

and the optimum energy expectation value is given by [13]

$$\mathscr{E}_c=E^0+E^2c\,, \tag{32}$$

$$c=\mu_{\text{opt}}=[(1+4A)^{1/2}-1]/2A\,. \tag{33}$$

For $A \ll 1$, the optimum scale

$$c=1-A+2A^2-5A^3+O(A^4) \tag{34}$$

which is closer to $a=1$ than to

$$b=1+A/2+A^2/4+A^3/8+O(A^4)\,. \tag{35}$$

In other words, $\Psi(1)=\Psi_a$ is closer to Ψ_c than $b\Psi(2)=\Psi_b$ is.

It should be noted that Löwdin-Adams perturbation theory is a special case of off-diagonal perturbation theory [15–20], which is rapidly convergent. Our special version enables us to calculate E^l up to $l=5$ with Φ and Ψ^1. Furthermore, scaling optimizes Ψ_μ[6]. Therefore, it comes as no surprise to us that $\mathscr{E}_c$ and E_{CI} are nearly equal, implying that

$$\Psi_c=\Phi+c\Psi^1 \tag{36}$$

is a good approximation to Ψ_{CI}.

In retrospect, we conclude that the incompleteness of the basis will always be with us, but that, under the circumstances, scaled Löwdin-Adams perturbation theory offers a simple method of performing perturbation-variation calculations.

3. Properties

In the language of double perturbation theory [6], a first-order property is given by

$$W=\sum_{l=0}^{\infty} E_1^l \tag{37}$$

where E_1^l are the usual double perturbation energies. In practice, however, one is usually interested in the partial sum

$$W(L)=\sum_{l=0}^{L} E_1^l \tag{38}$$

and the rate at which $W(L)$ converges to the true value W.

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[6] That scaling destroys the off-diagonal character is of no consequence to us.

Table 4. Dependence of E_1^1 on M[a]

	M	$Z=1$	$Z=2$	$Z=3$
$\pi\delta(\boldsymbol{r})$	1	0.14091418	0.72070990	1.71040353
	2	0.05607402	0.29822983	0.78114694
	3	0.01137329	0.29808759	0.88877695
	4	0.00335203	0.38044208	1.09089736
	5	0.00485270	0.40975885	1.12855726
r^{-2}	1	0.15377379	0.28292841	0.40365188
	2	0.08407537	0.09956563	0.15015495
	3	0.05910288	0.10669306	0.17618621
	4	0.05650216	0.12684974	0.20903827
	5	0.05727908	0.13436297	0.21537611
r^{-1}	1	0.01884817	0.00729520	0.00409594
	2	0.04214598	0.00739566	0.00418665
	3	0.05439919	0.00915727	0.00471175
	4	0.06018515	0.00915119	0.00486059
	5	0.06214652	0.00938989	0.00500160
r	1	+ 0.34473789	+0.02887344	+0.01047254
	2	− 0.88879252	−0.01836804	−0.00398844
	3	− 1,04130985	−0.01923813	−0.00397379
	4	− 1.15879726	−0.02030183	−0.00421061
	5	− 1.20504395	−0.02064395	−0.00425306
r^2	1	+ 5.3043732	+0.11257896	+0.02361926
	2	−14.9655430	−0.09820542	−0.01414030
	3	−14.0330680	−0.09704738	−0.01467317
	4	−15.9220001	−0.10266428	−0.01537313
	5	−16.5114792	−0.10359870	−0.01543590
r^3	1	+71.175160	+0.37241359	+0.04507257
	2	−233.597743	−0.43181411	−0.03827295
	3	−165.765636	−0.40955747	−0.04061260
	4	−204.693584	−0.41959925	−0.04074399
	5	−210.945436	−0.42221528	−0.04098535
r^4	1	+1004.23815	+1.26673092	+0.08788810
	2	−3825.79597	−1.86851447	−0.09854058
	3	−1875.73343	−1.71031045	−0.10604834
	4	−2854.18206	−1.65131200	−0.09970287
	5	−2885.89767	−1.68038082	−0.10166664

[a] See footnote in Table 2.

With the perturbed wavefunctions described above, we have calculated E_1^1 and E_1^2 for the operators $\mathscr{W}=\pi\delta(\boldsymbol{r})$ and r^m for $-2\leqq m\leqq 4$. The rate of convergence with respect to basis size, shown in Tables 4 and 5, can be regarded as fair.

For each property, we compute various approximations similar to those for the energy. The partial sums $W(L)$ are defined in Eq. (38); the other expectation values are

$$w(L)=\langle\Psi(L)|\mathscr{W}|\Psi(L)\rangle/\langle\Psi(L)|\Psi(L)\rangle\,, \tag{39}$$

$$w_\mu=\langle\Psi_\mu|\mathscr{W}|\Psi_\mu\rangle/\langle\Psi_\mu|\Psi_\mu\rangle\,, \tag{40}$$

Table 5. Dependence of E_1^2 on M[a]

	M	$Z=1$	$Z=2$	$Z=3$
$\pi\delta(\mathbf{r})$	1	−0.00011844	−0.02259430	−0.04742806
	2	0.02485253	−0.02773780	−0.06104219
	3	0.02427110	−0.02175037	−0.04904067
	4	0.01681581	−0.02442335	−0.04865689
	5	0.01301368	−0.02384171	−0.04726483
r^{-2}	1	−0.00490912	−0.02630929	−0.03288514
	2	0.01942160	−0.02766583	−0.03455419
	3	0.01804435	−0.02419795	−0.03090642
	4	0.01238722	−0.02672562	−0.03182588
	5	0.00922414	−0.02693608	−0.03172808
r^{-1}	1	−0.00277185	−0.00452607	−0.00347939
	2	−0.00305850	−0.00423823	−0.00307041
	3	−0.00138742	−0.00376957	−0.00293177
	4	−0.00136302	−0.00424647	−0.00307178
	5	−0.00179291	−0.00426779	−0.00306372
r	1	0.03130789	0.00315246	0.00087006
	2	0.34669395	0.00365930	0.00069030
	3	0.19049279	0.00310292	0.00080888
	4	0.18050659	0.00333128	0.00076751
	5	0.17222612	0.00314194	0.00074847
r^2	1	0.48904226	0.00956138	0.00150647
	2	7.77281128	0.01699080	0.00157517
	3	3.81190109	0.01361220	0.00199343
	4	3.82658197	0.01311505	0.00163119
	5	3.28368630	0.01217555	0.00160532
r^3	1	7.629747	0.02947628	0.00258639
	2	157.069395	0.08291862	0.00412649
	3	73.446136	0.06244738	0.00533584
	4	79.898681	0.05387495	0.00371262
	5	55.665746	0.05122461	0.00379842
r^4	1	127.25801	0.10281490	0.00497154
	2	3260.11234	0.04332267	0.01219638
	3	1632.20879	0.30664399	0.01573784
	4	1965.63567	0.24341324	0.00942366
	5	1001.15100	0.24793319	0.01029228

[a] See footnote in Table 2.

where $\Psi(L)$ and Ψ_μ have been defined in Eqs. (26) and (27). It can be shown that

$$w_\mu = E_1^0 + \mu[E_1^1 + \mu E_1^2]/(1 + \mu^2 A)\,. \tag{41}$$

The results (in atomic units) are presented in Tables 6–12, where the accurate values [21–24] are included for comparison. Obviously, these results confirm our expectation that Ψ_c leads to good values for w_c. The magnitude of the errors in w_c are 0.0047–0.111% for He (larger for H^-, and smaller for Li^+, as expected).

Table 6. $\mathscr{W} = \pi\delta(\boldsymbol{r})$

	$Z=1$	$Z=2$	$Z=3$
$W(0)=w(0)$	1.01256858	11.0033335	42.0115363
$W(1)$	1.01742128	11.4130924	43.1400936
$W(2)$	1.03043496[a]	11.3892507	43.0928288
$w(1)=w_a$	1.02947999	11.3872045	43.0903769
$w(2)=w_b$	1.03028382	11.3881559	43.0915450
w_c	1.02810731	11.3853255[a]	43.0880536[a]
W_{exact}	1.033904[b]	11.375248[c]	43.0523[d]

[a] Closest to W_{exact}.
[b] Ref. [23].
[c] Ref. [21].
[d] Ref. [22].

Table 7. $\mathscr{W} = r^{-2}$

	$Z=1$	$Z=2$	$Z=3$
$W(0)=w(0)$	2.18681908	11.9301632	29.6760768
$W(1)$	2.24409816[a]	12.0645262	29.8914529
$W(2)$	2.25332230	12.0375901	29.8597248
$w(1)=w_a$	2.24976765	12.0370205	29.8593084
$w(2)=w_b$	2.25165337	12.0372312	29.8594798
w_c	2.24645999	12.0366034[a]	29.8589672[a]
W_{exact}	2.233290[b]	12.034816[c]	29.85524[b]

[a] Closest to W_{exact}.
[b] Ref. [24].
[c] Ref. [21].

From the values of E_1^0, E_1^1, and E_1^2, it is straightforward[7] to derive the corresponding quantities in scaled perturbation theory (denoted by bars) for $\bar{h} = \mu^{-1} h$:

$$\bar{E}_1^0 = E_1^0\,, \tag{42}$$

$$\bar{E}_1^1 = \mu E_1^1\,, \tag{43}$$

$$\bar{E}_1^2 = \mu(1-\mu)E_1^1 + \mu^2 E_1^2\,, \tag{44}$$

$$\bar{W}(L) = \sum_{l=0}^{L} \bar{E}_1^l\,. \tag{45}$$

The setting of either $\bar{E}_1^2$ or $\partial\bar{W}(2)/\partial\mu$ to zero would lead to a geometric approximation [14, 26] for first-order properties

$$g = \mu_{\text{geom}} = [1 - (E_1^2/E_1^1)]^{-1}\,, \tag{46}$$

$$W_{\text{geom}} = E_1^0 + gE_1^1\,. \tag{47}$$

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[7] The reader may find the expressions, especially (22), in Ref. [25] helpful in the derivation.

Table 8. $\mathscr{W} = r^{-1}$

	$Z = 1$	$Z = 2$	$Z = 3$
$W(0) = w(0)$	1.32245140	3.37170170	5.37388911
$W(1)$	1.38459792	3.38109159	5.37889071
$W(2)$	1.38280501	3.37682380	5.37582699[a]
$w(1) = w_a$	1.37957907	3.37679664	5.37582260
$w(2) = w_b$	1.38100366	3.37679874	5.37582130
w_c	1.37704425[a]	3.37679233[a]	5.37582514
W_{exact}	1.3665240[b]	3.3766336[c]	5.37585[b]

[a] Closest to W_{exact}.
[b] Ref. [24].
[c] Ref. [21].

Table 9. $\mathscr{W} = r$

	$Z = 1$	$Z = 2$	$Z = 3$
$W(0) = w(0)$	6.22470734	1.87583733	1.14900216
$W(1)$	5.01966339	1.85519338	1.14474910
$W(2)$	5.19188951	1.85833532	1.14549757
$w(1) = w_a$	5.24709438	1.85842812	1.14550552
$w(2) = w_b$	5.22670894	1.85839047	1.14550241
w_c	5.28396887[a]	1.85850258[a]	1.14551171[a]
W_{exact}	5.420357[b]	1.8589446[c]	1.1455483[d]

[a] Closest to W_{exact}.
[b] Ref. [23].
[c] Ref. [21].
[d] Ref. [22].

Table 10. $\mathscr{W} = r^2$

	$Z = 1$	$Z = 2$	$Z = 3$
$W(0) = w(0)$	33.9934570	2.47571173	0.90622884
$W(1)$	17.4819778	2.37211303	0.89079294
$W(2)$	20.7656641	2.38428858	0.89239826
$w(1) = w_a$	21.4726993	2.38477333	0.89242962
$w(2) = w_b$	21.2420231	2.38456534	0.89241582
w_c	21.8954443[a]	2.38518439[a]	0.89245708[a]
W_{exact}	23.827404[b]	2.3869660[c]	0.8925580[d]

[a] Closest to W_{exact}.
[b] Ref. [23].
[c] Ref. [21].
[d] Ref. [22].

However, the geometric approximation has been applied almost exclusively to second-order properties in uncoupled Hartree-Fock perturbation calculations [26–29], and it is not clear if the approximation will work as well for first-order properties or for non-Hartree-Fock Φ. In any event, we refrain from generating more numerical values of $\bar{W}(2)$ for $\mu = a$, b, c, and g, because we believe that $\bar{W}(2)$ cannot compete with our w_c in terms of accuracy and reliability.

Table 11. $\mathscr{W} = r^3$

	$Z=1$	$Z=2$	$Z=3$
$W(0) = w(0)$	270.205377	4.29889084	0.91944732
$W(1)$	59.259941	3.87667556	0.87846197
$W(2)$	114.925687	3.92790017	0.88226039
$w(1) = w_a$	123.225500	3.92986726	0.88234471
$w(2) = w_b$	121.000574	3.92902811	0.88230701
w_c	127.401531[a]	3.93152582[a]	0.88241972[a]
W_{exact}	151.99878[b]	3.935886[b]	0.8825558[b]

[a] Closest to W_{exact}.

[b] Ref. [24].

Table 12. $\mathscr{W} = r^4$

	$Z=1$	$Z=2$	$Z=3$
$W(0) = w(0)$	2749.22897	9.37289383	1.15025512
$W(1)$	− 136.66870	7.69251301	1.04858848
$W(2)$	864.48230	7.94044620	1.05888076
$w(1) = w_a$	965.22338	7.94804140[a]	1.05908795
$w(2) = w_b$	947.40063	7.94493500	1.05899641
w_c	1000.95620[a]	7.95418364	1.05927010[a]
W_{exact}	1288.8438[b]	7.947056[b]	1.0592042[b]

[a] Closest to W_{exact}.

[b] Ref. [24].

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