

On definitions of L convergence of atomic correlation energies

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The two usual definitions of energy increments that characterize convergence of electronic energy calculations are shown to be numerically significantly different. In two special cases, helium and neon, their ratios are approximately 1.4. Care must be exercised when comparing calculations from separate sources lest differences of definition be interpreted physically.

I. INTRODUCTION

Accurate electronic wave functions usually mean large expansions. To evaluate, compare, determine convergence rates, and extrapolate large expansions, terms are often grouped together by mathematical or physical criteria, and the "contribution" of each group is individually examined. This paper concerns one such classification: " L limits" for atoms. The main point is that the numerical values of the energy increments of the two "natural definitions" in use, contrary to conventional expectation, are surprisingly different.

Convergence patterns of electronic energy calculations have been most thoroughly studied for the ground state of helium.¹⁻⁸ In 1962, Schwartz^{1,2} estimated the L increment (defined below in Sec. II) to the second-order energy to be

$$(-45/256)(L + \frac{1}{2})^{-4} = -0.176(L + \frac{1}{2})^{-4} \text{ a.u.}$$

In 1979, high-accuracy configuration interaction (CI) calculations⁵ gave an asymptotic variational L increment of $-0.074(L + \frac{1}{2})^{-4}$ a.u., down by a factor 2.4 from Schwartz. Recent accurate perturbational L increments through third order⁶ seem to be about 1.4 times the variational results. The discrepancy between "perturbation theory" and variational theory is the subject of this paper. One rationalization has attributed the difference to an "interference effect."^{7,8} What we demonstrate here is that the ratio of 1.4 is due mainly to the comparison of two *differently defined* sets of L increments.

Convergence patterns for the ground state of neon⁹⁻¹¹ have also been studied extensively both perturbationally and variationally and will serve as a second example. Convergence patterns for other atoms, e.g., beryllium,^{6,12} have also been studied, especially by perturbation theory, but the energy increments from variational calculations are not so complete as for helium or even neon.

The plan of the paper is as follows: In Sec. II we present the two different general definitions of L increments for closed-shell systems. In Sec. III we illustrate the numerical differences between these two definitions for helium and neon. In Sec. IV we show in detail for helium why the increments *must* be different. In Sec. V we make some concluding remarks.

II. TWO DEFINITIONS OF ENERGY INCREMENTS

Let a wave function ψ be written systematically as an orthogonal expansion in the form

$$\psi = \psi_{\text{ref}} + \psi_0 + \psi_1 + \dots \quad (1)$$

$\psi_{\text{ref}}, \psi_0, \psi_1, \dots$ are to be mutually orthogonal, and ψ_{ref} is to be normalized to unity, so that ψ has intermediate normalization: $\langle \psi_{\text{ref}} | \psi_{\text{ref}} \rangle = 1, \langle \psi_{\text{ref}} | \psi_L \rangle = 0$. We are principally concerned with the case that Eq. (1) represents a partial-wave expansion, but the discussion is pertinent to any orthogonal expansion.

$$\begin{aligned} \text{The energy can be similarly expanded, } E &= E_{\text{ref}} + \Delta E, \\ \Delta E &= \Delta E_0 + \Delta E_1 + \Delta E_2 + \dots \end{aligned} \quad (2)$$

The partition (1) for ψ does *not* lead to a unique partition (2) for ΔE . There are, however, two convenient definitions. One, for which we denote the energy increment ΔE_L by $\Delta E_{L,\text{in}}$, is suggested by the Schrödinger equation and intermediate normalization:

$$\Delta E = \langle \psi_{\text{ref}} | H | \psi_0 + \psi_1 + \dots \rangle, \quad (3)$$

$$\Delta E_L = \Delta E_{L,\text{in}} \equiv \langle \psi_{\text{ref}} | H | \psi_L \rangle. \quad (4)$$

The intermediate normalization definition is particularly germane to Rayleigh-Schrödinger perturbation theory (RSPT), in which the N th order energy can be written in the form, $E^{(N)} = \langle \psi_{\text{ref}} | H | \psi^{(N-1)} \rangle$. If the decomposition Eq. (1) for $\psi^{(N-1)}$ were substituted directly into this matrix element, we would obtain the corresponding decomposition of $E^{(N)}$ into L increments,

$$\Delta E_{L,\text{in}}^{(N)} = \langle \psi_{\text{ref}} | H | \psi_L^{(N-1)} \rangle, \quad (5)$$

which is in fact the definition used in the perturbation theory analyses of convergence patterns.^{1,2,6,10,11}

The second common type of definition is the difference between successive expectation values. Let $W(\psi)$ denote the energy expectation value

$$W(\psi) = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle. \quad (6)$$

Then define $\Delta E_{L,\text{ev}}$ by

$$\begin{aligned} \Delta E_L &= \Delta E_{L,\text{ev}} \\ &\equiv W(\psi_{\text{ref}} + \sum_{k=0}^L \psi_k) - W(\psi_{\text{ref}} + \sum_{k=0}^{L-1} \psi_k). \end{aligned} \quad (7)$$

The expectation-value style of ΔE_L is more germane to variational calculations.^{4,5,9}

Notice that $\Delta E_{L,\text{in}}$ depends explicitly on ψ_{ref} and on ψ_L , but not on any other ψ_k . In contrast, $\Delta E_{L,\text{ev}}$ depends explicitly on ψ_{ref} , on ψ_L , and also on ψ_0, ψ_1, \dots , and ψ_{L-1} . That is, $\Delta E_{L,\text{ev}}$ is dependent on the order in which the ψ_k appear in the wave function, whereas $\Delta E_{L,\text{in}}$ is not. In any event, both definitions give the same total:

TABLE I. Comparison of partial-wave energy increments for the ground state of the helium atom, in units of 10^{-6} hartree.

L	Variational calculation ^a		Perturbation theory ^b		$\Delta E_{L,\text{in}}/\Delta E_{L,\text{ev}}$
	$-\Delta E_{L,\text{ev}}$	$-\Delta E_{L,\text{in}}$	$-\Delta E_L^{(2)}$	$-(\Delta E_L^{(2)} + \Delta E_L^{(3)})$	
0	17 233.76	16 403.08	13 486	15 717	0.952
1	21 586.28	21 635.46	18 970	21 162	1.002
2	2 269.33	2 738.85	3 184	2 841	1.21
3	556.63	719.06	922	732	1.29
4	197.58	264.54	352	265	1.34
5	86.72	118.73	158	116	1.37
6	43.71	60.79	78	59	1.39
7	24.29	34.17	42	32	1.41
8	14.50	20.60	25	19	1.42
9	9.10	13.04	15	12	1.43
10	5.94	8.58			1.44
11	4.00	5.83			1.46

^aBased on the "O-limit" wave function of Ref. 5. The sum of the $\Delta E_{L,\text{ev}}$ is not quite equal the sum of the $\Delta E_{L,\text{in}}$ (error = 10^{-6} hartree) because the Hartree-Fock reference function was calculated in the full "2-9" basis (in which $E_{\text{HF}} = -2.861\,679\,33$ hartree) while the O limit wave function was given in a truncated natural orbital basis. See the text for details.

^bReference 6.

$$E = E_{\text{ref}} + \Delta E_{0,\text{in}} + \Delta E_{1,\text{in}} + \dots$$

$$= E_{\text{ref}} + \Delta E_{0,\text{ev}} + \Delta E_{1,\text{ev}} + \dots, \quad (8)$$

with $E_{\text{ref}} = W(\psi_{\text{ref}})$. In the next section, we show numerically for helium and neon that $\Delta E_{L,\text{in}}$ is quite different from $\Delta E_{L,\text{ev}}$.

III. NUMERICAL STUDY OF $\Delta E_{L,\text{in}}/\Delta E_{L,\text{ev}}$

In this section, we display the $\Delta E_{L,\text{in}}$ and $\Delta E_{L,\text{ev}}$ values for the ground states of helium and neon. For helium, the $\Delta E_{L,\text{in}}$ are available from both variational⁵ and RSPT⁶ calculations. For neon, the $\Delta E_{L,\text{in}}$ are available only from RSPT.¹⁰ The tables presented in this section demonstrate the systematic differences between the $\Delta E_{L,\text{ev}}$ and the $\Delta E_{L,\text{in}}$.

Helium provides the best illustration of the differences between $\Delta E_{L,\text{in}}$ and $\Delta E_{L,\text{ev}}$ because of the large number of values that are available from an extensive configuration interaction (CI) study⁵ of the ground state and from accurate third-order RSPT calculations⁶ of the $\Delta E_{L,\text{in}}$ based on a Hartree-Fock $\psi_{\text{ref}} = \psi_{\text{HF}}$. The partition (1) of the wave function in these studies is a partial-wave expansion. We let ψ_{ref} denote the Hartree-Fock wave function. The ψ_L denotes the contribution of all configurations involving only L -angular momentum orbitals, viz., of the type $(nL)(n'L)$. For $L = 0$, ψ_0 is the sum of all s -only configurations other than ψ_{ref} . The details of calculating the variational wave function and $\Delta E_{L,\text{ev}}$ are given in Ref. 5. The RSPT calculation is described in Ref. 6.

The values of the $\Delta E_{L,\text{ev}}$ were given in Tables III-V of Ref. 5, where they are referred to as "Total S," "Total P," "Total D," etc. for various size and quality basis sets constructed from piecewise-polynomial basis functions. There is some variation in each $\Delta E_{L,\text{ev}}$ with the enlargement of the basis in Ref. 5, but the variation is small compared with the differences with the corresponding $\Delta E_{L,\text{in}}$. The values for $\Delta E_{L,\text{ev}}$ listed here in Table I are taken from the single "O-limit" wave function, for which the maximum value of L was 11.

$\Delta E_{L,\text{in}}$ values were not given in Ref. 5. In the same piecewise-polynomial basis used for the "O-limit" wave function, we have calculated both the Hartree-Fock ψ_{ref} and the $\Delta E_{L,\text{in}}$'s, which we report here also in Table I. For $L > 5$, the ratio $\Delta E_{L,\text{in}}/\Delta E_{L,\text{ev}}$ is roughly 1.4, as can be seen from Table I.

The RSPT quantities $\Delta E_L^{(2)}$ and $\Delta E_L^{(2)} + \Delta E_L^{(3)}$ are also listed in Table I. It is evident numerically that the RSPT ΔE_L converge to the $\Delta E_{L,\text{in}}$, and not to the $\Delta E_{L,\text{ev}}$. The RSPT quantities were calculated by variation-perturbation methods using Slater-type basis functions, and we have taken them directly from Tables 1 and 3 of Ref. 6.

Neon provides a second example of ΔE_L values. The primary comparison, however, is not taken from a "complete" CI wave function for neon, but from one in which only the $2s$ and $2p$ electrons (and not the $1s$ electrons) were permitted to be excited, and then only with at most double excitations.⁹ For the neon calculations, ψ_L denotes the sum of all configurations obtained from the Hartree-Fock $1s^2 2s^2 2p^6$ by single and double excitations from $2s^2 2p^6$ that include at least one excited orbital with angular momentum L , and none higher. In Table II, we list $\Delta E_{L,\text{ev}}$ from Table IX of Ref. 9.

We remark that the label "calculated" in Table II means that the numbers are from STO-CI calculations, while "estimated" means extrapolated from the calculated values. (See Ref. 9 for details.) We note, moreover, that the $\Delta E_{L,\text{ev}}$ in Table II do not represent the difference in expectation values from a single truncated wave function, as in the case for helium in Table I, but instead between expectation values of separately optimized wave functions. The experience from helium⁵ is that the change on reoptimization is not consequential (especially as L increases), compared to the difference between $\Delta E_{L,\text{in}}$ and $\Delta E_{L,\text{ev}}$. We also note that for neon, we do not have $\Delta E_{L,\text{in}}$ values available from the variational calculation.

For comparison with the $\Delta E_{L,\text{ev}}$ values, we have listed in Table II the corresponding RSPT $\Delta E_L^{(2)}$, taken by combin-

TABLE II. Comparison of partial-wave energy increments to the correlation energy of the ($n = 2$) shell of the ground state of neon, in units of 10^{-5} hartree.

L	Variational calculation ^a		Perturbation theory ^b	
	$-\Delta E_{L,ev}$ (calc.)	$-\Delta E_{L,ev}$ (est.)	$-\Delta E_L^{(2)}$	$\Delta E_L^{(2)}/\Delta E_{L,ev}$ (est.)
1	13 560	13 563	14 102	1.04
2	11 086	11 093	11 291	1.02
3	3 414	3 423	3 486	1.02
4	1 245	1 258	1 392	1.11
5	407	424	542	1.27
6	171	190	254	1.34
7	81	115	137	1.19(1.37) ^c
8	38	56	76	1.4

^a Reference 9.

^b From Tables II, IV, and V of Ref. 10.

^c The result in parentheses is obtained by using the $L = 6$ extrapolation increment for $\Delta E_{7,ev}$ (est.). See discussion in the text and also Table IX of Ref. 9.

ing the results of Tables II, IV, and V of Ref. 10. Note that these are second-order energies. The third-order $\Delta E_L^{(3)}$ for neon are not known as accurately as those of second order, but unlike the helium case, they are relatively less important for neon.¹¹ Thus we take $\Delta E_L^{(2)}$ to be approximately equivalent to $\Delta E_{L,in}$.

We remark that the $\Delta E_{L,ev}$ are calculated with a much poorer basis than the $\Delta E_L^{(2)}$. Consequently, we have used the extrapolated $\Delta E_{L,ev}$'s rather than the calculated ones for direct comparison. However, the $L = 7$ extrapolation seems to be out of line from the others. In parentheses in Table II we have indicated what the extrapolated $\Delta E_{7,ev}$ and its ratio with $\Delta E_{L,in}$ would be if the "extrapolation increment" to $\Delta E_{L,ev}$ were the same as for $\Delta E_{6,ev}$ (cf. Table IX of Ref. 9). The ratio $\Delta E_L^{(2)}/\Delta E_{L,ev}$ (estimated) is in the approximate range 1.3 to 1.4 for $L > 5$, as can be seen from Table II.

IV. EXPLANATION

In this section, the reason why $\Delta E_{L,in}$ and $\Delta E_{L,ev}$ are so different for the ground state of helium is explained. Only helium is discussed, because for helium much of the treatment can be done analytically. If inequality is the rule for helium, then by inference inequality is the norm for other atoms and molecules. Note that the following "explanation" is heuristic: there are no claims for rigor.

At first it might seem surprising that $\Delta E_{L,in}$ and $\Delta E_{L,ev}$ are so different. For instance, if ψ were a *variational* wave function consisting of exactly two orthogonal terms, $\psi = \phi + \chi$, then because of the *variational* principle,

$$W(\psi) - W(\phi) = \langle \phi | H | \chi \rangle / \langle \phi | \psi \rangle, \quad (9)$$

and the two ΔE 's would be identical.

This observation is slightly misleading, as a more careful examination of $\langle \phi | H | \chi \rangle$ reveals. If one takes $\chi = \psi_L$ and $\phi = \psi_{HF} + \sum_{k=0}^{L-1} \psi_k$, then Eq. (9) becomes

$$\Delta E_{L,ev} = \frac{\langle \psi_{HF} | H | \psi_L \rangle + \sum_{k=0}^{L-1} \langle \psi_k | H | \psi_L \rangle}{1 + \sum_{k=0}^{L-1} \langle \psi_k | \psi_k \rangle} \neq \Delta E_{L,in}. \quad (10)$$

The right-hand side of Eq. (10) is not $\Delta E_{L,in}$. For helium it is not the denominator that is important: the overlap of the Hartree-Fock configuration (or alternatively the first natural orbital configuration) with the exact wave function is greater than 0.995, and as a consequence the denominator is different from 1 by only about 1%. The difference in the increments is dominated by the numerator:

$$\Delta E_{L,ev} \sim \langle \psi_{HF} | H | \psi_L \rangle + \sum_{k=0}^{L-1} \langle \psi_k | H | \psi_L \rangle, \quad (11)$$

$$\sim \Delta E_{L,in} + \sum_{k=0}^{L-1} \langle \psi_k | H | \psi_L \rangle. \quad (12)$$

To simplify the right-hand side of Eq. (11), we introduce the well-known, simple, correlated approximate wave function for helium, which has the form

$$\psi \sim (a + br_{12})\psi_{HF}, \quad (13)$$

or a more general, but similar form,

$$\psi \sim a\psi_{HF} + br_{12}\psi_{CI}, \quad (14)$$

where ψ_{CI} is a short CI expansion. In either case, it follows in three steps that $\Delta E_{L,in}/\Delta E_{L,ev} \sim 1/a$: (i) Replace H in Eq. (11) by $1/r_{12}$. Since only the two-electron term in the Hamiltonian can give a nonzero matrix element with ψ_L , this is exact:

$$\Delta E_{L,ev} \sim \langle \psi_{HF} + \sum_{k=0}^{L-1} \psi_k | 1/r_{12} | \psi_L \rangle. \quad (15)$$

(ii) Extend the summation limit from $L - 1$ to ∞ . The error introduced (see below) is $O(L^{-5})$, compared to $\Delta E_{L,ev}$ itself, which is $O(L^{-4})$:

$$\Delta E_{L,ev} \sim \langle \psi_{HF} + \sum_{k=0}^{\infty} \psi_k | 1/r_{12} | \psi_L \rangle, \quad (16)$$

$$\sim \langle \psi | 1/r_{12} | \psi_L \rangle. \quad (17)$$

(iii) Replace the exact wave function ψ in Eq. (17) by the approximation Eq. (13) [or Eq. (14)], and use the orthogonality $\langle \psi_{HF} | \psi_L \rangle = 0$ [or $\langle \psi_{CI} | \psi_L \rangle = 0$, for L greater than the largest "L" appearing in the "short" ψ_{CI}]:

$$\Delta E_{L,ev} \sim \langle (a + br_{12})\psi_{HF} | 1/r_{12} | \psi_L \rangle, \quad (18)$$

$$\sim a\langle \psi_{HF} | 1/r_{12} | \psi_L \rangle + b\langle \psi_{HF} | \psi_L \rangle, \quad (19)$$

$$\sim a \langle \psi_{\text{HF}} | 1/r_{12} | \psi_L \rangle, \quad (20)$$

$$\sim a \Delta E_{L,\text{in}}. \quad (21)$$

Thus,

$$\Delta E_{L,\text{in}} / \Delta E_{L,\text{ev}} \sim 1/a. \quad (22)$$

The value of a is not too sensitive to the precision of ψ_{HF} . For instance, if the Hartree-Fock orbital is approximated by a single Slater orbital,

$$\psi_{\text{HF}} \sim \pi^{-1} \zeta^{-3} \exp[-\zeta(r_1 + r_2)], \quad (23)$$

then the variationally obtained values are $\zeta = 1.8497$, $a = 0.3658$, and $a^{-1} \sim 1.4$. Using the more general approximation Eq. (14) and taking ψ_{CI} to consist of all the configurations that can be formed from the first three "s" natural orbitals and the first "p" natural orbital, again one obtains $a^{-1} \sim 1.4$. Both calculations are in agreement with the observed behavior for large L as listed in Table I.

An estimate of $\langle \psi_k | 1/r_{12} | \psi_L \rangle$, necessary to justify extending the upper summation limit in Eq. (16) to ∞ , can be made using Eq. (23) for ψ_{HF} and Eq. (13) for ψ . Then, by expanding¹³ r_{12} , one obtains for ψ_L :

$$\begin{aligned} \psi_L \sim & b \frac{4\zeta}{2L+1} \sum_{m=-L}^L Y_L^m(\theta_1, \phi_1) Y_L^m(\theta_2, \phi_2)^* \\ & \times \left(\frac{1}{2L+3} (r_</r_>)^2 - \frac{1}{2L-1} \right) r_>^L r_<^{1-L} \\ & \times \exp[-\zeta(r_1 + r_2)], \end{aligned} \quad (24)$$

where the Y_L^m , $r_<$, and $r_>$ have their usual meanings. By direct integration, one finds

$$\langle \psi_k | 1/r_{12} | \psi_L \rangle \sim bC [\min(k, L) + \frac{1}{2}]^{-2} \times [\max(k, L) + \frac{1}{2}]^{-4}, \quad (25)$$

$$\sum_{k=L}^{\infty} \langle \psi_k | 1/r_{12} | \psi_L \rangle = O(L^{-5}), \quad (26)$$

where C is of $O(1)$. The one loose end we do not try to tie is the quality of the approximation Eq. (13) or (14).

Thus, $\Delta E_{L,\text{in}} / \Delta E_{L,\text{ev}} \sim 1.4$ is a consequence of the two definitions and the " $(a + br_{12})\psi_{\text{HF}}$ " structure of ψ .

V. DISCUSSION

The two standard types of energy increments, given by the "intermediate normalization" formula and the "difference of expectation values" formula, are numerically significantly different. The ratio of the two for large L is approximately 1.4 in the helium and neon ground states. Although the motivation for both definitions is the same, the numerical consequences are not. For helium we have been able to relate the two definitions through an approximate, correlated wave function and to show that approximately 1.4 is to be expected. It would be interesting to know what the asymptotic ratio would be for other atoms and for excited states.

When comparing different quantum-mechanical calculations on the same atom or molecule, one must be careful to use consistent definitions for the energy increments. In particular, RSPT leads directly toward an "intermediate normalization" definition, whereas variational calculations lead more "naturally" to the difference of expectation values. We believe it preferable to regard the differences between the two as semantic, rather than as a physical interference effect.

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¹C. Schwartz, Phys. Rev. **126**, 1015 (1962).

²C. Schwartz, Meth. Comput. Phys. **2**, 241 (1963).

³C. F. Bunge, Theor. Chim. Acta **16**, 126 (1970).

⁴G. O. Morrell, Jr. and R. G. Parr, J. Chem. Phys. **71**, 4139 (1979).

⁵D. P. Carroll, H. J. Silverstone, and R. M. Metzger, J. Chem. Phys. **71**, 4142 (1979).

⁶K. Jankowski, D. Rutkowska, and A. Rutkowski, J. Phys. B **15**, 4063 (1982).

⁷M. R. Nyden and G. A. Petersson, J. Chem. Phys. **75**, 1843 (1981).

⁸G. A. Petersson and M. R. Nyden, J. Chem. Phys. **75**, 3423 (1981).

⁹F. Sasaki and M. Yoshimine, Phys. Rev. A **9**, 17 (1974).

¹⁰K. Jankowski and P. Malinowski, Phys. Rev. A **21**, 45 (1980).

¹¹K. Jankowski, D. Rutkowska, and A. Rutkowski, Phys. Rev. A **26**, 2378 (1982).

¹²C. F. Bunge, Phys. Rev. A **14**, 1965 (1976).

¹³See, for instance, Eqs. (13) and (32) of K. G. Kay, H. D. Todd, and H. J. Silverstone, J. Chem. Phys. **51**, 2359 (1969), or references cited therein.