it can be considered as an SCF equation for orthogonal energy localized orbitals. Whether, in practice, it is easier to solve directly for Eq. (41), instead of first solving for Eq. (39) and then applying the transformations described in the preceding sections, is questionable. It must also be borne in mind that Eq. (41) represents not only an equation for the SCF orbitals of maximal localization, but that it holds for the SCF orbitals of minimal localization as well.

COMPLEX LOCALIZED ORBITALS

Up to now all orbitals were assumed to be real, as is usually the case in molecules. Moreover the definition (42,ff) of the operator $\mathfrak{L}$ was purposely chosen such as to keep all quantities real.

If one abandons the convenience of reality, then the localization condition (9) becomes

$$[\varphi_n^*\varphi_n - \varphi_m^*\varphi_m|\varphi_n^*\varphi_m] = [\varphi_n^*\varphi_n - \varphi_m^*\varphi_m|\varphi_n\varphi_m^*] = 0\,, \quad (45)$$

and the transformation to localized orbitals is in general unitary. The kernel $L(\mathbf{x},\mathbf{x}')$ of the localization operator $\mathfrak{L}$ of Eq. (42) is now to be defined by

$$L(\mathbf{x},\mathbf{x}') = \sum_{n\neq m} \lambda_n(\mathbf{x})\lambda_m^*(\mathbf{x}')L_{nm}\,, \quad (46)$$

with

$$L_{nm} = \Lambda\{[\lambda_n^*\lambda_n - \lambda_m^*\lambda_m|\lambda_n^*\lambda_m]\} - (\lambda_n|\mathfrak{F}|\lambda_m)\,, \quad (46')$$

where $\Lambda\{z\}$ is now any complex function of the complex variable z, satisfying

$$\Lambda^*\{z\} = \Lambda\{-z^*\}\,,$$
$$\Lambda\{z\} = 0 \text{ only for } z = 0\,.$$

This guarantees that L_{nm} is a Hermitian matrix and, hence, $\mathfrak{L}$ a hermitian operator. The simplest choice is

$$L_{nm} = i[\lambda_n^*\lambda_n - \lambda_m^*\lambda_m|\lambda_n^*\lambda_m] - (\lambda_n|\mathfrak{F}|\lambda_m)\,. \quad (47)$$

It may be noted that the integral operator with the kernel

$$\lambda(\mathbf{x},\mathbf{x}') = i \sum_{n,m}{}' \lambda_n(\mathbf{x})\lambda_n^*(\mathbf{x}')[\lambda_n^*\lambda_n - \lambda_m^*\lambda_m|\lambda_n^*\lambda_m]$$

is the projection, on the space subtended by λ_1, $\lambda_2 \cdots \lambda_N$, of the integral operator with the kernel

$$\tilde{\lambda}(\mathbf{x},\mathbf{x}') = i \sum_n \lambda_n(\mathbf{x})\lambda_n^*(\mathbf{x}')\{U_n(\mathbf{x}') - U_n(\mathbf{x})\}\,,$$

where

$$U_n(x) = \int dV''\lambda_n^*(\mathbf{x}'')\lambda_n(\mathbf{x}'')/|\mathbf{x} - \mathbf{x}''|\,.$$

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Pair Correlation Energies*

LELAND C. ALLEN
Department of Chemistry, Princeton University, Princeton, New Jersey
ENRICO CLEMENTI
International Business Machines Corporation, Research Laboratory, San Jose, California
AND
H. M. GLADNEY†
Department of Chemistry, Princeton University, Princeton, New Jersey

I. INTRODUCTION

REALIZATION of a practical and easy-to-interpret theoretical formalism for electron-correlation effects is today the most actively pursued goal in the quantum mechanical description of atoms and molecules. The present article is an attempt to abstract from existing numerical data a set of empirical rules which can act as a guide to theoretical formulations of electron correlation.[1]

The correlation energy E_{corr} of an atomic or molecular system may be defined as the difference between the exact nonrelativistic energy and the Hartree–Fock energy for this system.[2] The nonrelativistic experimental energy can be obtained

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† Porter Ogden Jacobus Fellow, Princeton University, 1962–63.

[1] For other work on this problem see E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

[2] P. O. Löwdin, *Advances in Chemical Phys.*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. II, p. 207.

from spectroscopic data corrected for relativistic effects by perturbation methods. The relativistic effects are small for small atoms, but become increasingly important for increasing nuclear charge Z. Since the relativistic corrections are only imperfectly known (except for closed-shell systems) it is more convenient to carry through our analysis in terms of the "error energy" E_e defined as the difference between the Hartree–Fock result and the experimental total energy.

$$E_e \equiv E_{\text{corr}} + E_{\text{rel}} = E_{\text{HF}} - E_{\text{expt}} . \qquad (1)$$

Introduction of E_e is also useful in the comparison of atomic and molecular systems, because the relativistic effects in molecules are little changed from those in the constituent atoms.

If one starts with a Hartree–Fock solution as the zero-order many-electron wavefunction, then the Pauli principle plus the fact that the Hamiltonian contains no more than two particle operators implies that two-electron excitations will dominate electron-correlation effects. From computational experiments by many workers on a wide variety of systems[3,4] we know that these pair correlations are localized largely within a given shell and between electrons in the same immediate region of space. Further, since correlations are associated with pairs of orbitals rather than with pairs of electrons, the number of distinct pair correlations to be estimated is not $\frac{1}{2}N(N-1)$, as would be appropriate for a nonstructured N electron system, but of the order of N (e.g., the correlation between a $1s\alpha$- and a $2s\beta$-electron is equal to that between a $1s\beta$- and a $2s\alpha$-electron).

Examination of Table I and Fig. 1 confirms the qualitative picture given above. Whenever an electron is added to an ion, there is an increase in correlation and relativistic energy. The increase is large whenever a new electron pair is formed, but relatively small when an electron is put into an empty orbital. The increase in correlation energy on double occupation of a p orbital is larger than that on double occupation of a $1s$ orbital. For the $2s$-electrons, there is a strong Z dependency in the correlation energy, which was explained in terms of s,p degeneracy.[3] For the cases considered in this paper, the relativistic corrections are important for the $1s$-electrons, but may be treated as if they were negligible for $2s$- and $2p$-electrons. Were relativistic corrections for $2p$-electrons important, the curves for the p-electrons would diverge as the nuclear charge increased, rather than being approximately parallel. For the first three p-electrons, there is only a small increase in E_e, which is interpreted mainly as correlation with inner-shell electrons, and to a lesser extent as correlation among the $2p$-electrons and relativistic effects of the $2p$-electrons.

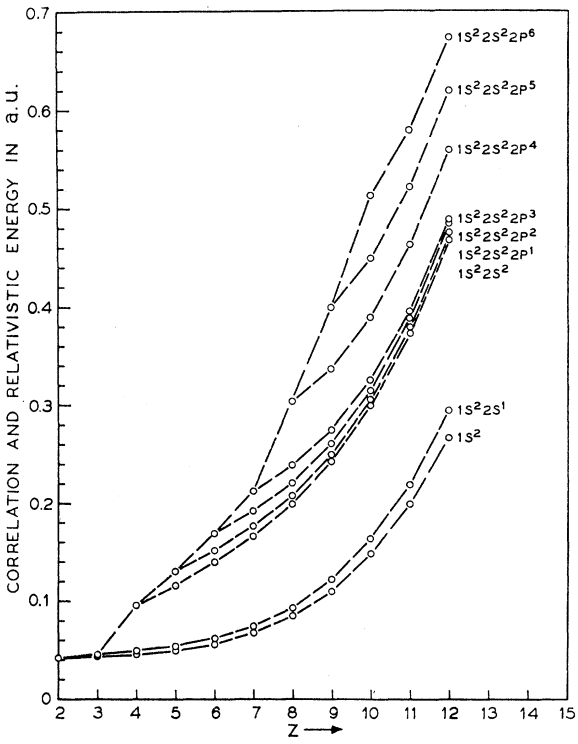

FIG. 1. Error energy vs Z for $2 \leq N \leq 10$.

Fröman[5] has made limited tests of the hypotheses that only correlations between electrons in the same orbital are important and that the correlation energy per doubly filled orbital is constant. The correlation energy of the $2s$-electrons in beryllium is nearly the same as that of a pair of $1s$-electrons, but the equality is not preserved for higher members of the isoelectronic sequence. Arai and Onishi[6] tested the hypothesis that correlation energy was an additive function of pairs of electrons. However, their single determinant wavefunctions were not Hartree–Fock solutions, but rather crude hydrogenic functions with only one variational parameter apiece; they made no distinction between electron pairs of like and of opposing spin and altogether ignored rela-

[3] J. Linderberg and H. Shull, J. Mol. Spectr. **5**, 1 (1960).
[4] L. C. Allen and A. M. Karo, Rev. Mod. Phys. **32**, 275 (1960).
[5] A. Fröman, Phys. Rev. **112**, 870 (1958); Rev. Mod. Phys **32**, 317 (1960).
[6] T. Arai and T. Onishi, J. Chem. Phys. **26**, 70 (1957).

TABLE I. Atomic correlation and relativistic energies.[a,b]

Atomic configuration and state	Nuclear charge Z	Experimental energy[c]	Hartree–Fock energy[d]	Correlation and relativistic energy
$K2s^22p^6 - {}^1S_0$	12	-199.50_4	$-198.830\ 5$	0.67_3
	11	-162.25_6	$-161.676\ 8$	0.57_9
	10	-129.06_0	$-128.547\ 0$[f]	0.51_3
$K2s^22p^5 - {}^2P_{1.5}$	12	-196.55_9	$-195.940\ 3$	0.61_9
	11	-160.51_9	$-159.997\ 2$	0.52_2
	10	-128.26_8	$-127.817\ 8$	0.45_0
	9	$-\ 99.809$	$-\ 99.409\ 3$[f]	0.40_0
$K2s^22p^4 - {}^3P_2$	12	-192.54_2	$-191.982\ 7$	0.55_9
	11	-157.88_6	$-157.423\ 5$	0.46_3
	10	-126.76_2	$-126.371\ 9$	0.39_0
	9	$-\ 99.169$	$-\ 98.831\ 6$	0.337
	8	$-\ 75.113$	$-\ 74.809\ 4$[f]	0.304
$K2s^22p^3 - {}^4S_{1.5}$	12	-187.34	$-186.860\ 4$	0.48_9
	11	-154.25_1	$-153.855\ 2$	0.39_6
	10	-124.43_0	$-124.104\ 1$	0.32_6
	9	$-\ 97.884$	$-\ 97.608\ 9$	0.275
	8	$-\ 74.612$	$-\ 74.372\ 6$	0.239
	7	$-\ 54.614$	$-\ 54.400\ 90$[f]	0.213
$K2s^22p^2 - {}^3P_0$	12	-180.486	$-179.999\ 7$	0.486
	11	-149.160	$-148.770\ 5$	0.389
	10	-120.859	$-120.543\ 5$	0.315
	9	$-\ 95.581$	$-\ 95.319\ 6$	0.261
	8	$-\ 73.321$	$-\ 73.100\ 2$	0.221
	7	$-\ 54.080$	$-\ 53.889\ 97$	0.192
	6	$-\ 37.857\ 4$	$-\ 37.688\ 61$[f]	0.168 8
$K2s^22p - {}^2P_{0.5}$	12	-172.208	$-171.732\ 7$	0.476
	11	-142.826	$-142.446\ 3$	0.380
	10	-116.217	$-115.910\ 8$	0.306
	9	$-\ 92.377$	$-\ 92.126\ 8$	0.250
	8	$-\ 71.303$	$-\ 71.094\ 7$	0.208
	7	$-\ 52.992$	$-\ 52.815\ 78$	0.176
	6	$-\ 37.443\ 6$	$-\ 37.292\ 21$	0.151 4
	5	$-\ 24.659\ 1$	$-\ 24.529\ 05$[f]	0.130 0
$K2s^2 - {}^1S_0$	12	-162.434	$-161.966\ 1$	0.468
	11	-135.162	$-134.788\ 4$	0.374
	10	-110.411	$-110.111\ 0$[e]	0.300
	9	$-\ 88.177$	$-\ 87.934\ 0$[e]	0.243
	8	$-\ 68.457$	$-\ 68.257\ 7$[e]	0.199
	7	$-\ 51.248$	$-\ 51.082\ 31$[e]	0.166
	6	$-\ 36.547\ 5$	$-\ 36.408\ 50$[e]	0.139 0
	5	$-\ 24.354\ 4$	$-\ 24.237\ 58$[e]	0.116 8
	4	$-\ 14.669\ 35$	$-\ 14.573\ 02$[e,f]	0.096 33
$K2s - {}^2S_{0.5}$	12	$-150.379\ 8$	$-150.084\ 6$	0.295 2
	11	$-125.452\ 2$	$-125.232\ 8$	0.219 4
	10	$-102.793\ 9$	$-102.631\ 1$[e]	0.162 8
	9	$-\ 82.401\ 4$	$-\ 82.279\ 49$[e]	0.121 9
	8	$-\ 64.271\ 3$	$-\ 64.178\ 04$[e]	0.093 3
	7	$-\ 48.400\ 8$	$-\ 48.326\ 85$[e]	0.073 9
	6	$-\ 34.787\ 7$	$-\ 34.726\ 06$[e]	0.061 6
	5	$-\ 23.430\ 06$	$-\ 23.375\ 99$[e]	0.054 07
	4	$-\ 14.326\ 73$	$-\ 14.277\ 40$[e]	0.049 33
	3	$-\ 7.478\ 57$	$-\ 7.432\ 727$[e,f]	0.045 84
$1s^2 - {}^1S_0$	12	$-136.877\ 61$	$-136.611\ 1$	0.266 5
	11	$-114.434\ 73$	$-114.236\ 1$	0.198 6
	10	$-\ 94.008\ 88$	$-\ 93.861\ 12$[e]	0.147 7
	9	$-\ 75.596\ 92$	$-\ 75.486\ 13$[e]	0.110 79
	8	$-\ 59.195\ 990$	$-\ 59.111\ 15$[e]	0.084 84
	7	$-\ 44.803\ 611$	$-\ 44.736\ 16$[e]	0.067 45
	6	$-\ 32.417\ 592$	$-\ 32.361\ 19$[e]	0.056 40
	5	$-\ 22.036\ 064$	$-\ 21.986\ 23$[e]	0.049 83
	4	$-\ 13.657\ 444$	$-\ 13.611\ 30$[e]	0.046 14
	3	$-\ 7.280\ 413$	$-\ 7.236\ 415$[e]	0.043 998
	2	$-\ 2.903\ 784$	$-\ 2.861\ 680$[e]	0.042 104

[a] Energies in this and subsequent tables in atomic (Hartree) units. To convert to cm^{-1} multiply by $2\ R_M$, where R_M is the Rydberg constant appropriate to the nucleus in question (Reference 22).

[b] Mass-polarization corrections (References 12, 23) of the order of 10^{-5} atomic units have been ignored in the Hartree–Fock results.

[c] Reference 11.

[d] Reference 25.

[e] Reference 13.

[f] Reference 24.

tivistic effects. We shall show that, in fact, there is an approximate additivity rule, in which correlations between electrons paired in the same orbital are the principal contributions. It also turns out that relativistic mass effects are effectively important only for s-electrons.

Recent calculations by Sharma and Coulson and by Knight and Scherr[7] of correlation energies for the $1s2s^3S$ and ^1S excited states of an atom of nuclear charge Z have been particularly useful in confirming the qualitative prediction that electrons in different spatial orbitals will have a correlation small compared to that for two electrons in the same orbital. In addition, electrons of parallel spin should have especially low-correlation energy, since the exchange effects between electrons of parallel spin are accounted for in the Hartree–Fock method. The results are

For the triplet level:

$$E_{\text{corr}}(1s\alpha,2s\alpha) = 0.002231 - (0.002747/Z) + O(1/Z^2)\ ; \tag{2a}$$

For the singlet level:

$$E_{\text{corr}}(1s\alpha,2s\beta) = 0.010842 - (0.024098)/Z + O(1/Z^2)\ . \tag{2b}$$

These results should be contrasted with the corresponding equation for the ground state.[8,9]

$$E_{\text{corr}}(1s\alpha,1s\beta) = 0.046652 - (0.009590)/Z + O(1/Z^2)\ . \tag{2c}$$

The correlation energy of the two excited states is much less than that of the ground state, and that of the triplet state much less than that of the singlet excited state.

II. ANALYSIS AND RESULTS

The procedure for making a decomposition of the correlation energy has been to adopt a set of hypotheses and then attempt a trial decomposition to see if this produces an internally consistent analysis of the data. The hypotheses given below are the most useful and successful in this type of 'self-consistent' decomposition. The degree to which the rules are general, as well as the limitations on the analysis imposed by incomplete knowledge and accuracy, are discussed in this section.

(a) There are approximately N distinct pair correlations where N is the number of electrons in the atom. Pair correlations are additive.

(b) For any given nuclear charge, the contribution for any pair of orbitals does not depend on N.

TABLE II. Correlations in the $2s$ shell.

	Uncorrected for intershell correlations		Corrected for intershell correlations	
Z	$E^0_{\text{corr}}(2s,2s)$	$0.014Z - 0.004$	$E_{\text{corr}}(2s,2s)$	$0.012_5Z - 0.011$
4	0.050	0.052	0.038	0.039
5	0.067	0.066	0.051	0.052
6	0.082	0.080	0.064	0.064
7	0.097	0.094	0.079	0.077
8	0.109	0.108	0.089	0.089
9	0.124	0.122	0.104	0.102
10	0.136	0.136	0.116	0.114
11	0.149	0.150	0.127	0.127
12	0.160	0.160	0.138	0.139

(c) Intershell correlation energies are negligible. (The smaller vertical intervals in Fig. 1 are a measure of the failure of this hypothesis and corrections to it are discussed below.)

Fröman[5] has estimated the correlation energies for a pair of $1s$-electrons over a range of the nuclear charge parameter and finds them remarkably constant at about 1.19 eV. The same result was reported earlier by Shull and Löwdin[10] and is substantially confirmed in more recent calculations.[8,9,11–13]

$$E'_{\text{corr}}(2s,2s) = E_e(1s^2 2s^2) - E(1s^2) - 2E_{\text{rel}}(2s) \approx 0.014Z - 0.004\ . \tag{3}$$

(See the first two columns of Table II.[14]) $E'_{\text{corr}}(2s,2s)$ is the correlation contribution when the $K-L$ correlation is neglected. This relatively small interaction between shells can be deducted yielding

$$E_{\text{corr}}(2s,2s) \approx E'_{\text{corr}}(2s,2s) - 2E_{\text{corr}}(2s\alpha,1s\alpha) - 2E_{\text{corr}}(2s\alpha,1s\beta)\ . \tag{4a}$$

The result (Table II, column 3) is given by the

[7] C. S. Sharma and C. A. Coulson, Proc. Phys. Soc. (London) **A80**, 81 (1962). These calculations have been repeated and corrected by R. E. Knight and C. W. Scherr [R. E. Knight, Ph.D. thesis, University of Texas, 1962 (unpublished)]. We have used the Knight and Scherr values.

[8] J. Linderberg, Phys. Rev. **121**, 816 (1961).

[9] E. A. Hylleraas and J. Mitdal, Phys. Rev. **103**, 829 (1956).

[10] H. Shull and P. O. Löwdin, J. Chem. Phys. **25**, 1035 (1956).

[11] C. W. Scherr, J. N. Silverman and F. A. Matsen, Phys. Rev. **127**, 830 (1962).

[12] C. L. Pekeris, Phys. Rev. **112** 1649 (1958); Phys. Rev. **115**, 1216 (1959).

[13] C. C. J. Roothaan, L. M. Sachs and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1962).

[14] We adopt the following notation: $E_{\text{rel}}(2s)$ is the relativistic correction of a $2s$-electron; $E_{\text{corr}}(2s\alpha,2p\beta)$ is the correlation correction for the pair of orbitals indicated; $E_e(1s^2 2s)$ is the total error energy for the configuration $1s^2 2s$. There should be no ambiguity since E_{rel} is used only with respect to a single orbital, E_{corr} only with respect to pairs of orbitals and E_e only for observed total error energies.

formula

$$E_{\text{corr}}(2s,2s) \approx 0.012_5 Z - 0.011 \,. \qquad (4b)$$

Linderberg and Shull[3] have calculated energy lowerings for 3- and 4-electron systems by configuration interaction. They found a very small $1s - 2s$ correlation[15] and a $2s$-correlation energy linear in the nuclear charge. Their Z coefficient is 0.0117, in good agreement with Eq. (4). These authors attribute the linear term to orbital degeneracy in the limit of infinite Z, and tabulate states of larger atoms expected to have such a term. These include the ground states of 4- to 8-electron atoms, but not those for 2-, 3-, 9-, or 10-electron atoms. Presently existing data are not precise enough for a conclusive test of these predictions, but it does appear that the linear term is associated explicitly with the $2s$-electrons.

Our present data have sufficient precision to make a fairly detailed analysis of the breakdown of rule (c). The correlation and relativistic energy of a $2s$-electron with the completed K shell may be estimated from Table I and the same quantity may also be obtained from Sharma and Coulson's calculations [Eq. (2)] yielding a direct test of additivity. We expect

$$E_e(1s^2 2s) - E_e(1s^2) \approx E_{\text{corr}}(1s\alpha,2s\alpha) + E_{\text{corr}}(1s\beta,2s\alpha) + E_{\text{rel}}(2s) \,. \qquad (5a)$$

The first two terms on the right are available in (2a) and (2b), respectively. The first two columns of Table III compare the members of (5a) and we

TABLE III. Correlation of a lone $2s$-electron with the K shell.[a]

Z	$E_{\text{corr}}(1s\alpha,2s\beta) + E_{\text{corr}}(1s\beta,2s\beta) + E_{\text{rel}}(2s)$	$E_e(1s^2 2s) - E_e(1s^2)$ (observed values)	$E_{\text{corr}}(1s\alpha,2s\beta) + E_{\text{rel}}(2s)$
3	0.00416	0.00184	0.00284
4	0.00643	0.00319	0.00488
5	0.00784	0.00424	0.00616
6	0.0091	0.0052	0.0073
7	0.0104	0.0064	0.0086
8	0.0122	0.0085	0.0103
9	0.0148	0.0111	0.0129
10	0.0185	0.0151	0.0166
11	0.0238	0.0208	0.0218
12	0.0306	0.0287	0.0286

[a] See text for details; the first and third columns are derived from the relativistic corrections of Table VII and Eq. (2); the second column is directly from Table I.

find that the right-hand side is uniformly too large, because a secondary effect has been overlooked. This is the Pauli exclusion principle correlation of the valence electron with one core electron, which keeps the valence electron further from the core than it would be otherwise. $E_{\text{corr}}(1s\beta,2s\alpha)$ is reduced from the value (2b). As an approximate correction we may reduce the estimate of $E_{\text{corr}}(1s\beta,2s\alpha)$ by the correlation energy of the parallel spin pair, $E_{\text{corr}}(1s\alpha,-2s\beta)$. Then

$$E_e(1s^2 2s) - E_e(1s^2) \approx E_{\text{corr}}(1s\alpha,2s\beta) + E_{\text{rel}}(2s) \,. \qquad (5b)$$

The right-hand side of (7b) appears in the third column of Table III. The agreement with the observed values is considerably improved. It is *as if* the correlation of parallel-spin electrons were negligible. The decomposition above is supported by recent work by Kelly[16] on Be using the many-body diagrammatic perturbation theory of Goldstone and by Watson[17] and Weiss[18] using a many configuration treatment. The Watson function has been analyzed in terms of pairwise correlations by Sinanoğlu.[19] Kelly finds a $(1s,1s)$ correlation of 1.15 eV, $(2s,2s)$ correlation of 1.19 eV, and a $(1s,2s)$ correlation of 0.135 eV. Since the error in his correlation energy calculation is 0.11 eV these results agree almost exactly with ours. The intershell correlation energy in Kelly's work is 6% of the total and in Watson's work it is 5%.

TABLE IV. Correlation energies for $2p$-electrons.

Z	$E_e(2p^6) - E_e(2p^5)$	$E_e(2p^5) - E_e(2p^4)$	$E_e(2p^4) - E_e(2p^3)$
8			0.065
9		0.063	0.062
10	0.063	0.060	0.064
11	0.057	0.059	0.067
12	0.063	0.060	0.070
	Mean 0.063 a.u. ± 0.004 a.u.		

Correlation of the p-electrons presents a simpler problem than that of the $2s$-electrons. If we make assumption (c), the estimate of the correlation of paired $2p$-electrons is simply

$$E_{\text{corr}}(2p\alpha,2p\beta) \approx E_e(1s^2 2s^2 2p^m) - E_e(1s^2 2s^2 2p^{m-1}) \quad (m = 4,5,6) \,. \qquad (6)$$

In Table IV are listed these differences and we see that the assumption of constant correlation energy

[15] Cf. Eq. (2) from the results of Coulson and Sharma and Knight and Scherr. This conclusion is illustrated in Fig. 1 by the small value of $E_e(1s^2 2s) - E_e(1s^2)$.

[16] H. P. Kelly, Ph.D. thesis, University of California, Berkeley, 1962 (unpublished), UCAL–10471. Phys. Rev. (to be published).

[17] R. E. Watson, Phys. Rev. **119**, 170 (1960).

[18] A. W. Weiss, Phys. Rev. **122**, 1826 (1961).

[19] O. Sinanoğlu, J. Chem. Phys. **36**, 706 (1962).

per doubly filled orbital is quite reasonable. The estimate, 0.063 ± 0.004 a.u. (1.71 eV) is 43% greater than the correlation in the $1s$ orbital. Because of assumption (c), however, this estimate does include some correlation between p orbitals and the core.

Estimates of the correlations of p-electrons with p-electrons in orthogonal orbitals ($E_{\text{corr}}(p,p')$) and with the core of s-electrons ($E_{\text{corr}}(p,core)$) are available in the data for four- to seven-electron atoms. However, the present data are insufficient to permit separation of $2p - 2s$ effects from $2p - 1s$ effects. We have

$$E_{\text{corr}}(p,core) \approx E_e(1s^2 2s^2 2p) - E_e(1s^2 2s^2) \,, \quad (7a)$$

$$E_{\text{corr}}(p\alpha,p'\alpha) \approx E_e(1s^2 2s^2 2p^2) - 2E_e(1s^2 2s^2 2p) + E_e(1s^2 2s^2) \,, \quad (7b)$$

$$E_{\text{corr}}(p\alpha,p'\alpha) \approx \tfrac{1}{2}\,[E_e(1s^2 2s^2 2p^3) - E_e(1s^2 2s^2 2p^2) - E_e(1s^2 2s^2 2p) + E_e(1s^2 2s^2)] \,. \quad (7c)$$

These estimates appear in Table V. The data are not precise enough to support detailed analysis, but it is clear that both p-core correlation and $p\alpha - p'\alpha$ correlation decrease as Z increases. The individual contributions are small, but *in toto* constitute a not negligible portion of the total correlation energy. An important datum not obtained in our present analysis is the correlation of a p-electron with an orthogonal p-electron of opposite spin, $E_{\text{corr}}(p\alpha,p'\beta)$. We expect $E_{\text{corr}}(p\alpha,p'\beta) > E_{\text{corr}}(p\alpha,p'\alpha)$, but the correlation of a $2p$-electron with a doubly filled $2p$ orbital will probably be smaller than the sum of $E(p\alpha,p'\alpha)$ and $E(p\alpha,p'\beta)$ just as $E_e(1s^2 2s) - E_e(1s^2)$ was less than the sum of the correlations estimated for the excited helium atom states. Because of these uncertainties, it is best to use the uncorrected $E_{\text{corr}}(p,p)$.

TABLE V. Secondary p-electron correlations.

Z	$E_{\text{corr}}(p,\text{core})$[a] Eq. (7a)	$E_{\text{corr}}(p\alpha,p'\alpha)$ Eq. (7b)	$2E_{\text{corr}}(p\alpha,p'\alpha)$ Eq. (7c)	$E_{\text{corr}}(p\alpha,p'\alpha)$[b]
5	0.013			
6	0.012	0.005		(0.005)
7	0.010	0.006	0.011	0.006
8	0.009	0.004	0.009	0.004
9	0.007	0.004	0.007	0.004
10	0.006	0.005	0.005	0.003
11	0.006	0.003	−0.001	0.001
12	0.008	0.002	−0.005	0.000

[a] "Core" here denotes the set of four s-electrons.
[b] Mean values.

III. SOURCES OF DATA AND RELATIVISTIC EFFECTS

In Table I appear interpolated total electronic energies, Hartree–Fock energies and the correlation and relativistic decrements, for atoms and ions of two to ten electrons, nuclear charge two to twelve and infinite nuclear mass. The interpolated total energies are taken from the results of Scherr, Silverman and Matsen.[11] Directly observed experimental ionization potentials[20] for multiply charged ions are unreliable or often unavailable. These authors employ the well-known perturbation expansion

$$E^{(N)}(Z) = Z^2 \sum_{i=0}^{\infty} \mathcal{E}_i^{(N)} Z^{-i}$$

for the eigenvalues of the nonrelativistic Schrödinger equation for N electrons about a nucleus of charge Z. Similar series are obtained for ionization potentials by differencing the series for $E^N(Z)$ and $E^{(N-1)}(Z)$. The first two coefficients are available theoretically and the third to fifth coefficients are estimated using the first three experimental ionization potentials[21] of each atom. The extrapolated ionization potentials are combined with the very accurate variational energies obtained by Pekeris[12] for the helium sequence. These new results are more reliable than previous ones based on empirical extrapolations.[20,21] The data may be converted to values for any specific nuclear mass simply by multiplication by the appropriate Rydberg factor.[22] Mass polarization corrections[23] are included in the interpolated energies[11,12] but not in the Hartree–Fock energies. For helium-like ions, these range[12] from about 2×10^{-5} atomic units for nuclear mass 4 to about 4×10^{-5} atomic units for nuclear mass 20; they have a negligible effect on the correlation estimates of Table I.

The atomic Hartree–Fock energies are taken from recent calculations by Roothaan, Sachs, and Weiss,[13] by Clementi, Roothaan, and Yoshimine[24] and by Clementi.[25] These calculations are based on Roothaan's formulation of the open-shell, self-consistent-field equations.[26]

Although not entirely satisfactory, extant studies[5,11,12] of relativistic corrections are sufficient for

[20] *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Govt. Printing Office, Washington, D. C., 1949).
[21] B. Edlén, J. Chem. Phys. **33**, 98 (1960).
[22] See references 11 or 12 for values of the Rydberg factor $2R_M$ appropriate to the most common isotopes.
[23] H. A. Bethe and E. E. Salpeter, in *Handbuch der Physik*, edited by S. Flügge (Springer–Verlag, Berlin, 1957), Vol. 25, Part 1, p. 252.
[24] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).
[25] E. Clementi, J. Chem. Phys. **38**, 996 (1962).
[26] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

TABLE VI. Relativistic corrections for Mg ions (in a.u.).

Number of electrons	$E_{rel}(1s)$	$E_{rel}(2s)$	$E_{rel}(2p)$	E_{rel}(total)	E_{rel}(S.S.M.[11])	ΔE
2	0.2351	...	...	0.2351	0.2206	0.0145
3	0.2346	0.0288	...	0.2364	0.2430	0.0204
4	0.2336	0.0533	...	0.2869	0.2611	0.0258
5	0.2319	0.0495	0.0095	0.2909	0.2754	0.0155
6	0.2315	0.0460	0.0170	0.2945	0.2870	0.0075
7	0.2306	0.0422	0.0228	0.2956	0.2830	0.0126
8	0.2298	0.0391	0.0268	0.2957	0.2790	0.0167
9	0.2291	0.0365	0.0296	0.2952	0.2750	0.0202
10	0.2292	0.0343	0.0315	0.2951	0.2714	0.0237

our ends. Fröman[5] has emphasized that relativistic corrections are important only for inner electrons. Hartmann and Clementi,[27,28] using the method of Fröman,[5] repeated and extended the perturbation calculation for the relativistic correction to the closed shell isoelectronic series with 2,4,10,12,18, 20,30, and 36 electrons and to open-shell configurations for 1st- and 2nd-period atoms and ions.

In Table VI are reported the individual relativistic corrections for the $1s$,$2s$, and $2p$ electrons for the Mg^{10+} ion up to the Mg^{2+} ion. Of the ions discussed in this paper, Mg has the highest nuclear charge and is the case for which relativistic corrections are most important. Table VI indicates clearly that the $1s$-electrons are of predominant importance and that the $2s$ are more important than the $2p$. It is to be noted that for the neutral Mg atom, the $3s$ contribution to the relativistic energy is 0.0014 a.u., which should be compared with computed contributions 0.2280, 0.0344, and 0.0312 for the $1s$-, $2s$-, and $2p$-electrons. The second last column lists the semiempirical relativistic energies[11] and the final column the difference between computed and empirical relativistic corrections. The agreement is consistently better than 90%. By subtraction in column two of Table VI of the first entry of the last column of the same table (the ΔE value of 0.0145), one can bring the computed values into essential agreement with the empirical data. This procedure is equivalent to a supposed calculation of the $1s$ contribution of the relativistic energy with exact wavefunctions, and the $2s$ and $2p$ contributions with Hartree–Fock functions. This procedure is entirely reasonable in view of the predominant importance of the $1s$ electrons in relativistic effects.

Scherr, Silverman, and Matsen[11] adopted the relativistic corrections of Pekeris[12] for the K-shell and used a semiempirical scheme to estimate the corrections for L-shell electrons. Assuming that the relativistic energy can be decomposed into summable one-electron contributions, they fitted Dirac equation eigenvalues (modified by nuclear charge shielding parameters) to $^2P_{\frac{1}{2}} - {}^2P_{\frac{3}{2}}$ optical doublet data, for the Li-, Be-, and F-isoelectronic sequences. In Table VII we quote selected values from their work and

[27] H. Hartmann and E. Clementi, Phys. Rev. (to be published).
[28] E. Clementi, J. Mol. Spectr. (to be published).

Table VII. Relativistic corrections for closed shells.[a,b]

				Single $1s$-electron		Single $2s$-electron		Single $2p$-electron	
Z	2 electrons	4 electrons	10 electrons	$E_{rel}(1s)$	Eq. (9a)	$E_{rel}(2s)$	Eq. (9b)	$E_{rel}(2p)$	Eq. (9c)
2	5.993×10^{-5}			2.996×10^{-5}	2.957×10^{-5}				
3	4.999×10^{-4}			2.499×10^{-4}	2.360×10^{-4}				
4	1.878×10^{-3}	1.918×10^{-3}		0.939×10^{-3}	0.902×10^{-3}	0.070×10^{-3}	0.02×10^{-3}		
5	5.092	5.350		2.546	2.534	0.134	0.146		
6	1.135×10^{-2}	1.225×10^{-2}		0.568×10^{-2}	0.568×10^{-2}	0.045×10^{-2}	0.048×10^{-2}		
7	2.217	2.458		1.109	1.112	0.120	0.120		
8	3.940	4.442		1.970	1.976	0.251	0.251		0.001×10^{-2}
9	6.520	7.457		3.260	3.267	0.468	0.472		0.006
10	1.021×10^{-1}	1.184×10^{-1}	1.197×10^{-1}	0.511×10^{-1}	0.511×10^{-1}	0.815	0.810	$0.02_2 \times 10^{-2}$	0.027
11	1.528	1.792	1.837	0.764	0.763	0.132×10^{-1}	0.130×10^{-1}	0.07_5	0.076
12	2.207	2.611	2.714	1.103	1.099	0.198	0.200	0.17_2	0.17
13	3.090	3.685	3.906	1.545	1.536	0.302	0.294	0.36_9	0.35
14	4.217	5.065	5.443	2.108	2.091	0.424	0.427	0.63_0	0.61
15	5.628	6.803	7.389	2.814	2.789	0.588	0.576	0.97_7	1.02

[a] References 11 and 12.
[b] See Eq. (9) of the text for the analytic fits to the data.

that of Pekeris. If the relativistic correction for inner-shell electrons were independent of the presence and number of outer electrons, half the difference between the correction for four electrons and that for two would be a reasonable estimate of $E_{\mathrm{rel}}(2s)$. An estimate of $E_{\mathrm{rel}}(2p)$ may be obtained similarly. These values are fit with expressions of the form used by Scherr, Silverman, and Matsen[11]:

$$E_{\mathrm{rel}}(2s) \approx 2.14 \times 10^{-6}(Z - 2.1_0)^4 , \quad (9a)$$

$$E_{\mathrm{rel}}(2p) \approx 2.14 \times 10^{-6}(Z - 6.6_5)^4 . \quad (9b)$$

In Table VII are included both the direct estimates and the values from (9). These formulas are, of course, invalid when the right-hand side tends to zero, and in any event are only true to first order. Inner-shell relativistic corrections are not independent of the existence of electrons in outer shells and since the $1s$ screening constant is reduced by the presence of outer electrons these outer electrons will in fact contain relativistic corrections.[29] However, when considering the total collection of electrons in a system our analysis shows that the various contributions may be treated *as if* the relativistic corrections were negligible. Since the shielding constants of Scherr, Silverman, and Matsen do not depend on the quantum number l (but only on j), our result should not be greatly affected by shielding effects. It should also be pointed out that the Hartree–Fock calculations are carried out in the nonrelativistic limit characterized by the quantum number L and S and thus it might be more appropriate to compare the theoretical total energies with experimental values obtained by statistically weighting the ground-state multiplet structure energies rather than the lowest experimental energy as we have done. Numerical investigation, however, indicates that this does not appreciably alter the analysis, since the cases considered are well described in the $L - S$ coupling scheme.

We have found in the previous section that the correlation energy associated with a pair of $2p$-electrons is about 0.06 a.u.; Table VII shows that for $Z < 12$ the relativistic correction for a p-electron may be taken as negligible. For $2s$-electrons, the effective relativistic correction is an order-of-magnitude larger and cannot be disregarded for $Z > 6$. The relativistic correction for $1s$-electrons is five to ten times larger than that for $2s$-electrons.

IV. CONCLUSION

The analysis of numerical data we have presented in this paper shows that the long-desired separability and additivity of pair correlations in atoms and ions is in fact true with reasonable and practical accuracy for many chemical problems. A combination of empirical rules for pair correlations and relativistic energies also make it possible to state with good accuracy the energy differences between Hartree–Fock total energies and the often difficult-to-obtain total experimental energy. The empirically derived rules may be stated as:

Pair Correlation Energies

I. The correlation energy is additive in pairs of electrons of opposite spin, with the major contribution arising from pairs occupying a single orbital. The much smaller but still present correlation of opposite spin electrons in different orbitals is not independent of the presence of a second electron in one of the orbitals, because the Pauli exclusion principle acts to reduce the effective value of these contributions if one orbital is doubly occupied.

II. The correlation energy for a pair of $1s$-electrons is nearly independent of nuclear charge and equal to 1.19 eV.

III. The correlation energy for a pair of $2s$-electrons is a linear function of Z (e.g., 1.63 and 3.51 eV for $Z = 6$ and 10, respectively.).

IV. The correlation energy for a pair of $2p$-electrons is nearly independent of nuclear charge and equal to 1.7_1 eV.[30] [This value of $E_{\mathrm{corr}}(2p\alpha,2p\beta)$ is not corrected for interorbital effects.]

V. The small correlations between p-electrons and inner-shell electrons and between p-electrons in different orbitals decrease with increasing Z. We have not obtained complete estimates of these relatively small effects, because we do not have estimates of $E_{\mathrm{corr}}(2p\alpha,2p'\beta)$. Presumably, certain excited multiplets of the ground atomic configurations may be used to obtain accurate estimates, and this is being investigated at present.

Relativistic Energies

I. Relativistic energies are additive for doubly occupied orbitals. This is confirmed by the values of E_e listed in Table I. Relativistic energies should also be roughly additive for single orbitals since a major part of the correction is the expectation of a one-electron term in the Hamiltonian.[11]

II. Relativistic corrections occur mainly in the s orbitals and there principally in the $1s$ orbital.

[29] J. N. Silverman (private communication) and C. W. Scherr (private communication).

[30] This value is remarkably close to that obtained from much cruder arguments by L. C. Allen, J. Chem. Phys. **34**, 1156 (1961).

The contribution to the 1s-orbital energy is five to ten times greater than that to the 2s-orbital energy. For single electrons in doubly filled orbitals, the relativistic corrections are approximately:

$$E_{\mathrm{rel}}(1s) \approx 0.116_8\alpha^2(Z - .534)^4, \quad (9a)$$

$$E_{\mathrm{rel}}(2s) \approx 0.0402\alpha^2(Z - 2.1_0)^4, \quad (9b)$$

$$E_{\mathrm{rel}}(2p) \approx 0.0402\alpha^2(Z - 6.6_5)^4. \quad (9c)$$

These values appear in Table VII together with the results of Pekeris[12] and Scherr *et al.*[11] from which they were derived. (These contain the implicit assumption, only true to first order, that the correction for an inner electron is independent of the presence of an outer one.)

The additivity of pair correlation effects here demonstrated by the analysis of instrumental and computational experiments on atomic systems is of first importance to contemporary formulations of the many-electron problem in atoms and molecules. The traditional method of configuration interaction is most efficiently carried through and interpreted under the assumption of additivity.[31] In addition to other factors, successful utilization of the recent formulations of Sinanoğlu,[19,32] Szász,[33] and Tsang[34] depends upon the separability and additivity of pair correlations. A description of correlation in terms of opposite spin pairs is also inherent to the method of spin-correlated orbitals.[35] Further, it seems evident that, in the generalized self-consistent-field theory of McWeeny,[36] the localized electron groups which are to be treated exactly should be groups of two orbital partners. The present analysis also suggests, for calculations in the near future, the additional approximation of neglecting all correlations except those between orbitally paired electrons. Such a treatment would account for more than 80% of the total correlation energy.

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Nonadiabatic Theory for Diatomic Molecules and Its Application to the Hydrogen Molecule*

W. Kołos†

Laboratory of Molecular Structure and Spectra, Department of Physics, The University of Chicago, Chicago, Illinois

AND

L. Wolniewicz

Department of Theoretical Physics, Nicholas Copernicus University, Toruń, Poland

1. INTRODUCTION

One of the most fundamental approximations[1] of the theory of molecular structure consists of separating the nuclear motion and in computing only the electronic wave functions and energies for fixed positions of the nuclei. This is the socalled adiabatic approximation which is applicable, if the motion of the nuclei is much slower than that of the electrons. In the mathematical formulation of this approximation, the total wave function is assumed in the form of a product both of whose factors can be computed as solutions of two separate Schrödinger equations.

In most applications the separation is valid with sufficient accuracy, and the adiabatic approach is extremely valuable, especially if the electronic properties of molecules are considered. However, as

* Supported in part by the National Science Foundation.
† Permanent and present address: Institute of Nuclear Research, Polish Academy of Sciences, Warsaw, Poland.
[1] M. Born and R. Oppenheimer, Ann. Phys. **84**, 457 (1927).