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Inter- and Intra-atomic Correlation Energies and Theory of "Core-Polarization"

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ABSTRACT

A generalized second order perturbation treatment based on the use of all Slater determinants that can be formed from a complete one electron basis set is given for a many electron system whose zero order wave function is a single determinant of Hartree-Fock (H.F.) orbitals. The correlation energy of the system is broken down into the energies of pairs of electrons including exchange. Also some non-pairwise additive terms arise which represent the effect of the other electrons on the energy of a correlating pair on account of the Pauli exclusion principle. All energy components are written in approximate but closed forms involving only the initially occupied H.F. orbitals. Then each term acquires a simple physical interpretation and becomes adoptable for semi-empirical usage. The treatment is applied in detail to two particular problems: a) The correlation energy between an outer electron in any excited state and the core electrons, e.g. in the Li atom, is represented by a potential acting on the outer one. This potential can be regarded as the mean square fluctuation of the Hartree-Fock potential of the core, and applies even when the outer electron penetrates into the core. The magnitudes of some of the correlation effects are calculated for Li. b) Starting from a complete one electron basis set of SCF MO's, the energy of a molecule is separated into those of

ABSTRACT

(continued)

groups of electrons and *intra*-molecular dispersion forces acting between these groups. The assumptions that are usually made in discussing dispersion forces at such short distances are then removed and generally applicable formulae are given. In the last section some three or more-electron correlation effects, and limitations inherent in the use of "many electron group functions" for overlapping systems are discussed.

Inter- and Intra-atomic Correlation Energies and Theory of "Core-Polarization"

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I. Introduction

Although the total energy of a many electron system is well approximated by the Hartree-Fock (H.F.) method,[1,2] the remaining error, i.e. the difference between the complete self-consistent field (SCF) H.F. solution and the exact solution of the many electron non-relativistic hamiltonian, is usually of the order of chemically interesting quantities. This error, unless otherwise indicated, will be taken here as the precise definition[2] of "correlation energy." In recent years considerable effort has been devoted to obtaining more accurate solutions by the use of "configuration-interaction," i.e. expansion of a many electron wave function in terms of

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[1] For reviews see: D. R. Hartree, Calculation of Atomic Structures, Wiley and Sons, New York, 1957, and

[2] P. O. Löwdin in Advances in Chemical Physics, Vol. II, Interscience Publishers, New York, 1959; pp. 207-ff.

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a basis set of one electron functions.[2] Computers now allow much progress for simpler systems (e.g. molecules from the first row of the periodic table) in spite of slow convergence; nevertheless it is desirable and often necessary to use the formal structure of quantum mechanics to develop schemes that are amenable to simple physical interpretation and generalization as well as towards well defined semi-empirical methods for complicated systems.

One such scheme for treating certain correlation effects that is of interest from several aspects has arisen in the theory of atomic spectra under the name of "core polarization."[1] In alkali-like configurations most optical transitions occur by the excitation of a "series" electron outside an inner "core" giving a hydrogen-like spectrum. Although H.F. SCF method takes the average effect of the outer orbital on the core into account, the correlation between the instantaneous position of the series electron and the core is not included. As we shall see below, it has long been thought that this correlation energy can be represented by an additional effective potential acting on the outer electron. Such an approach offers several advantages from the semi-empirical point of view. If this potential can be determined from the first few observed levels, then "correlation" corrections to higher levels can be obtained[3] by taking appropriate expectation values. Hartree[1,4] has summarized the various

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[3] A. S. Douglas, Proc. Cambridge Phil. Soc., 52, 687 (1956).

[4] D. R. Hartree, Repts. on Progr. in Physics XI, 113 (1946).

attempts that have been made at obtaining such a potential semi-empirically. The form of this potential at large separations is given by $-A/r^4$, with $\underline{A}$ proportional to the polarizability of the inner core, and $\underline{r}$ the distance of the series electron from the nucleus, as can be seen from a classical argument. Several quantum mechanical derivations have been given for this potential (see Section II), but these all require the outer electron to be far from the core, in high, "non-penetrating" orbits, and omit various exchange effects. The need for the clarification of the form and feasibility of a potential for penetrating orbitals has been emphasized by Hartree.[1,4] This need becomes most acute in connection with another application: In molecules where the inner cores can be assumed to be quite unchanged by the binding, the correlation energy between the cores and the valence electrons can be obtained with the use of the potential derived from atomic spectra. Such an application is also implied in the "Π-electron" approximation[5] in organic molecules.

A very much related problem concerns the correlation energy between electron groups which may be considered to be centered around different nuclei. At large separations, this correlation energy leads to the familiar London "dispersion" attraction[6,7] between two atoms in their

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5. Pariser and Parr, J. Chem. Phys. <u>21</u>, 466 (1953).

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6. F. London, Z. Physik. Chem., <u>B11</u>, 222 (1930).
7. H. Margenau, Revs. Mod. Phys., <u>11</u>, 1 (1939).

ground states. (In this case, the above definition of "correlation energy" is somewhat altered, but still applies if the electrons of one system are considered to move in the self-consistent field of the other.) The derivation of London energy aside from requiring the atoms to be non-overlapping also makes use of a multipole expansion and taking only the dipole-dipole term into account necessitates the atoms to be small compared to their internuclear distance, R. The importance of London type forces not only at large separations, but even within the various regions of the same molecule has also been recognized and have been used to estimate the "correlation energies" between the lone-pair electrons in the halogen series to explain the anomalous binding energy variation going from F_2 to I_2, and to account for the isomerization energies of hydrocarbons.[8] Exactly the same difficulties that are involved in the representation of inner-outer shell correlations by effective potentials however are also present in this London-type approach and are again principally due to: a) Use of multipole expansions at short distances; b) Neglect of exchange; c) Neglect of the "exclusion" of certain virtual transitions of the correlating electrons to levels already occupied by other electrons; and d) Use of different basis sets for different electrons.

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[8] K. S. Pitzer, Advances in Chemical Physics, Vol. II, Interscience Publishers, New York, 1959; pp. 59 ff.

Some of these difficulties have already been mentioned by Coulson.[9] The connection between the two problems presented above becomes more apparent when the correlation energy between two separated atoms is written similar to an effective potential without making multipole expansions, as will be shown in the last section of this article or by viewing the "correlation energy" between co-centric shells as a Van der Waals' - like "dispersion" energy. The latter view has recently been taken by McWeeny who based his treatment on anti-symmetrized products of many electron group functions satisfying generalized orthogonality conditions.[10] As it will be discussed below, however, these conditions are too restrictive and do not circumvent some of the difficulties already listed.

To treat the two well known problems presented above and similar correlation effects from a unified point of view, in the next section of this article we shall give a generalized second order perturbation theory of a many electron system whose zero order wave function is a single Slater determinant of Hartree-Fock orbitals. The perturbation method will be based on the use of all "ordered configurations" that can be formed from a

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[9] C. A. Coulson, in *Symposium on Hydrogen Bonding, Ljubljana, 1957*, Pergamon Press, New York (1959); p. 349

[10] R. McWeeny, Proc. Roy. Soc. (London), *253A*, 242 (1959).

complete one electron basis set.[2] By a systematic classification of all the virtual transitions represented by these "ordered configurations," the correlation energy of a system will be broken down into electron pair correlations including exchange and non-pairwise additive "exclusion" terms. Definition of "mean excitation energies" for each pair will allow the approximate evaluation of both the pair energies and "exclusion" effects using only the occupied spin-orbitals. The approach has many applications and also provides a link with the recent "many-body" methods[11] developed in different fields of physics. A large portion of this article will be devoted to the "core-polarization" problem, not only because it is of interest in itself, but also because a system with a "series" electron is more general than a system of closed shells and the excited as well as the ground state of the former can be treated as well. Detailed derivations will be given for convenience with specific reference to the lithium atom although generalization to any other appropriate atom or molecule is straightforward. In Section II, a correlation potential will be derived and shown to be the "mean square fluctuation" of the Hartree-Fock potential acting on an electron. Section III will give the "exclusion" effect of an outer orbital, e.g. in Li, on the correlation energy of the core (Li^+) itself

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[11] For a brief introduction see:

D. ter Haar, Introduction to the Physics of Many-body Systems (Interscience Publishers, Inc., N. Y., 1958).

In Section IV, numerical magnitudes of some of these effects will be calculated for Li and the "core-polarization" potential compared with earlier ones. In Section V molecules are discussed in general and both the use of intra-molecular "dispersion" energies and "core-polarization" justified eliminating the usual approximations mentioned above by starting from a complete one electron basis set of molecular orbitals, SCF MO's. In the last section, some higher order correlation effects are mentioned; a "dispersion" energy formula including such effects, but for use only with asymptotic intermolecular forces is derived and the use of "generalized antisymmetrized products" of many electron group functions[10] is discussed.

II. Theory of "Core-Polarization"

The correlation energy between two electrons one of which is firmly bound to a nucleus and the other is in an orbital with high quantum numbers, as in the excited states of He, can be represented by an effective potential determined by the inner, i.e. "core" electron and acting on the outer one if one approximates the exact two electron wave functions by:

$$\psi_k (r_1, r_2) = u_c (r_1; r_2) u_v^k (r_2) \qquad (1)$$

where r_1, r_2 refer to the coordinates of inner and outer electrons respectively, u_v^k's are the various states of the outer electron and $u_c(r_1; r_2)$ describes the "core" electron and depends only parametrically on r_2. This "adiabatic approximation" [‡] is very similar to the Born-Oppenheimer separation of nuclear and electronic motions in molecules. Since the outer electron is much less tightly bound than the inner one, by virial theorem it can be considered to move slowly compared to the latter. Then, the energy of the core can be determined for various fixed values of r_2, thus depending on it parametrically and it in turn acts as a potential energy for the motion of the outer electron. This approach

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[‡] I am indebted to Professor W. T. Simpson for a stimulating discussion on this approach.

has been applied to highly excited states of *He* by Bethe[12] treating the stationary charge at r_2 as a perturbation on $u_c^0(r_1)$, the free "core" function. The same approach has been extended to Li, Na and K atoms in their ground states by Callaway[13] neglecting the penetration and the nearness of the valence electrons to the cores. Veselov and Bersuker[14] have also considered the alkali, but obtained $u_c(r_1;r_2)$ variationally. The adiabatic approach suffers from the difficulties that were outlined in the introduction. Especially for the ground states of the alkali the valence electron penetrates into the core considerably, and near the nucleus or the other electrons it can no longer be considered moving slowly. Moreover, since the basic concept of the approach is fundamentally opposed to the

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[12] H. A. Bethe, in *Handbuch der Physik* (Edwards Brothers, Ann Arbor, 1943), Vol. *24*/1, pp. 339 ff.; see also: Bethe and Salpeter, *Encyclopedia of Physics*, Vol. *35*, (Springer-Verlag, Berlin 1957) pp. 223 ff.

[13] J. Callaway, Phys. Rev., *106*, 868 (1957).

[14] G. Veselov and I. B. Bersuker, Vestnik Leningrad Univ. Ser. Fiz. Khim., No. 16, 55 (1957);
I. B. Bersuker, Optika i Spektrosk., *3*, No. 2, 97 (1957).

indistinguishability of the electrons, some exchange effects can be brought[15] in only artificially and other "exclusion" effects which we shall discuss would be difficult to introduce.

Another approach which shows the connection between inter-atomic London "dispersion" forces and the correlation energy between core and valence electrons more clearly has been taken by Mayer and Mayer[16] and Van Vleck and Whitelaw.[17] They used conventional second-order perturbation theory with hydrogen-like orbitals for the outer electron and considered only "non-penetrating orbits" where again r_2 is assumed to be always larger than r_1. Exchange effects are excluded and the dipole term in the multipole expansion introduces the polarizability of the "point-core." Thus none of the treatments just outlined give a sufficient basis for the improvement of the Hartree-Fock solutions for "series" electrons by the use of

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15. G. Ludwig, Helv. Physica Acta, 7, 273 (1934).

16. J. E. and M. G. Mayer, Phys. Rev., 43, 605 (1933).

17. J. H. Van Vleck and N. G. Whitelaw, Phys. Rev., 44, 551 (1933).

effective potentials especially near the core.[1,4]

For use in a more general theory of "core-polarization" as well as in many other applications to be discussed in subsequent sections of this article, we shall now proceed to a generalized perturbation treatment of a many electron system whose wave function in zero order can be represented by a single Slater determinant. Structures containing either all closed shells or closed shells plus an outer electron are such systems. All exchange effects will be included and in second order, the correlation energy of the system will be broken down into correlation energies of pairs and non-pairwise additive "exclusion" terms. The feasibility of expressing the correlation energy involving an "outer electron" by an effective potential for any state will be examined and such potentials will be derived quite generally.

The basic theorem[2] of the method of "superposition of configurations" is that if $\left\{ u_k(\underset{\sim}{x}) \right\}$ form a complete orthonormal basis set for the space of a single electron ($\underset{\sim}{x}$ including both spatial and spin coordinates), then any anti-symmetric N electron function can be expanded as:

$$\psi(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \ldots \underset{\sim}{x}_N) = \sum_{K}^{\infty} C_K \, \Phi_K(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \ldots \underset{\sim}{x}_N) , \qquad (2)$$

where Φ_K represents the normalized Slater determinants:

$$\Phi_K(\underset{\sim}{x}_1, \underset{\sim}{x}_2, \ldots \underset{\sim}{x}_N) = (N!)^{-1/2} \det \left\{ u_{k_1}, u_{k_2}, \ldots u_{k_N} \right\} \qquad (3)$$

and K runs over every unique selection of the one electron indices $k_1 < k_2 < \ldots < k_N$, i.e. all "ordered configurations."[2] In this representation the energy eigenvalues are the solutions of the secular equation:

$$\left| \underset{\sim}{H} - E \underset{\sim}{I} \right| = 0 \qquad (4)$$

with $\underset{\sim}{H} = \left\{ < \psi_K \mid H \mid \psi_L > \right\} = \left\{ < K, H \quad L > \right\}$ and $\underset{\sim}{I}$ the unit matrix. If any one of the non-degenerate ψ_K in Eq. (2), say, ψ_a, is chosen as the first approximation to ψ, then E can be written[2] rigorously as the solution of

$$E = H_{aa} + \underset{\sim}{H}_{ab} \left(E \underset{\sim}{I}_{bb} - \underset{\sim}{H}_{bb} \right)^{-1} \underset{\sim}{H}_{ba} \qquad (5)$$

where the matrix $\underset{\sim}{H}$ has been partitioned into four submatrices. A great variety of perturbation methods can be derived[18] from Eq. (5) by making various approximations in the exact remainder after taking H_{aa} as the "unperturbed" energy. Thus if the off-diagonal elements of $\underset{\sim}{H}_{bb}$ are neglected and E replaced by H_{aa}, a Schrödinger type generalized perturbation equation is obtained. This equation was first given by Epstein:[19]

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[18] See also:

Riesenfeld and K. M. Watson, Phys. Rev., 104, 492 (1956).

[19] P. S. Epstein, Phys. Rev., 28, 695 (1926); see also: Pauling and Wilson, *Introduction to Quantum Mechanics*, (McGraw Hill Book Co., N. Y., 1935)

$$E_{\mu} \approx H_{MM} - \sum_{K \neq M} \frac{H_{MK} H_{KM}}{H_{KK} - H_{MM}} = H_{MM} + E_{M}^{(2)} , \qquad (6)$$

Here among all the diagonal elements of $\underset{\sim}{H}$, H_{MM} is assumed to be the closest to the exact eigenvalue E_{μ}. In the summation, K covers the entire orthonormal many electron basis set such as in Eq. (2), except Ψ_{M}. Equation (6) is particularly convenient to use[20,21] when the one electron basis set consists of Hartree-Fock functions, because then all H_{MK} in which K differs from M by only one spin-orbital vanish. Also because of the orthonormality of $\left\{u_{k}\right\}$ only double excitations contribute to the sum in Eq. (6).

Now consider a system of closed shells and an outer electron which incorporates the features of closed shells that we wish to examine (see Section V) in addition to the effective potential problem. For purposes of the latter we define the following one electron basis set: The first (N-1) spin-orbitals $u_{1}, u_{2}, \ldots u_{(N-1)}$ are obtained from a complete H.F. SCF solution of the closed shell part (N-1 electrons) of the system after stripping the outer electron. If we are interested in say n +1 states of the outer electron, then the next n + 1 orbitals u_{N}, $u_{N+1} \ldots u_{N+n}$ will

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[20] R. K. Nesbet, Proc. Roy. Soc. (London), A230, 312 (1955).

[21] Reference 2, pp. 283 - 285.

be taken as the solutions of the H. F. equation for an electron in the field of the already determined fixed "core". The rest of the basis set may be completed[21] in some way by, e.g., a Schmidt orthogonalization process. The complete basis set of spin-orbitals thus obtained will now be denoted by $\left\{ u_k(\underset{\sim}{x}) \right\} = \left\{ \underline{k} \right\} = 1, 2, 3, \ldots$ all odd integers meaning spin-orbitals with spin $\underline{\alpha}$, and all even integers those with spin $\underline{\beta}$. For concreteness and convenience we now continue the treatment on the simplest case, the Li atom, although extension to larger systems is straight-forward. For any state $(1/(3!)^{1/2})$ det $(1s_\alpha \, 1s_\beta \, u_{k\alpha})$ or $\overline{\text{det}}$ (12k) of Li, the first few spin-orbitals by our choice satisfy the equations:

$$h_1^{\circ} \, 1s(\underset{\sim}{r}_1) + \left(\int |1s\,(\underset{\sim}{r}_2)\,|^2 \; r_{12}^{-1} \; d\,\tau_2 \right) 1s\,(\underset{\sim}{r}_1) = \epsilon_{1s} \, 1s(\underset{\sim}{r}_1) \tag{7}$$

where

$$h_1^{\circ} = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} \tag{8}$$

and

$$h^{\text{eff}}_{\text{core}} \, u_k = h_1^{\circ} \, u_k(\underset{\sim}{r}_1) + 2\left(\int |\, 1s(\underset{\sim}{r}_2)\,|^2 \, r_{12}^{-1} \, d\,\tau_2\right) u_k(\underset{\sim}{r}_1) - \left(\int 1s^*(\underset{\sim}{r}_2) u_k(\underset{\sim}{r}_2) r_{12}^{-1} \, d\tau_2\right) 1s(\underset{\sim}{r}_1)$$

$$= \epsilon_k \, u_k \, (\underset{\sim}{r}_1)$$

for $u_{k\alpha} = k > 3$. The second order correlation energy is given by Eq. (6) in conjunction with Eq. (2) and the one electron basis set just defined. To separate this energy into parts, all the ordered configurations that would give non-vanishing matrix elements in Eq. (6) can be classified according to which one or two spin-orbitals of the initial state $\overline{\text{det}}$ (12k) have been replaced to give the particular configuration. Consider first the ground state $\overline{\det}$ (123), i.e. $\frac{1}{\sqrt{6}}$ det $(1s_\alpha\ 1s_\beta\ 2s_\alpha)$. From this state, keeping in mind that the indices $\underline{k}_1$, $\underline{k}_2$, $\underline{k}_3$ which make up $\underline{K}$ in Eq. (2) must satisfy the condition $\underline{k}_3 > \underline{k}_2 > \underline{k}_1$ ($\underline{k}_1$ = 1 to ∞), the following types of virtual excitations are possible:

Single excitations:

$$\begin{array}{lllll} 1, 2, 3 & \longrightarrow & 1, 2, \ell & \ell > 3 & (9) \\ & \longrightarrow & 1, k, 3 & k > 3 & \\ & \longrightarrow & m, 2, 3 & m > 3 & \end{array}$$

Double excitations:

$$\begin{array}{lllll} 1, 2, 3 & \longrightarrow & 1, k, \ell & \ell > k > 3 & (10) \\ & \longrightarrow & m, 2, \ell & \ell > m > 3 & \\ & \longrightarrow & m, k, 3 & k > m > 3 & \end{array}$$

all higher excitations $\underline{\ell} > \underline{k} > \underline{m} > 3$ giving $\underline{H}_{OK} = 0$. We have labeled the indices differently depending on which initial orbitals remain unchanged. The first thing to notice is that with our choice of the orbitals all $\underline{H}_{OK}$ for the single virtual excitations of the <u>outer</u> electron[†] vanish by

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[†] Because of complete anti-symmetry we cannot refer to a definite electron. What we mean by "outer" electron is <u>any</u> one of the electrons occupying the particular <u>orbital</u>, 3.

the generalized[21] Brillouin theorem; i.e.

$$H_{OK} = < \overline{\det}\,(123),\ H\,\overline{\det}\,(12\,\ell) > = < \ell,\ h^{eff}_{core}\ 3 > = \epsilon_3 < \ell,\ 3 > = 0;\ (\ell \neq 3).$$

On the other hand single excitations from the core and double excitations lead to:

$$\begin{aligned} &< \overline{\det}\,(123),\ H\,\overline{\det}\,(1k3) > = < \overline{\det}\,(23),\ g_{12}\ \overline{\det}\,(k3) > \\ & \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (12) \\ &< \overline{\det}\,(123),\ H\,\overline{\det}\,(m23) > = < \overline{\det}\,(13),\ g_{12}\ \overline{\det}\,(m3) > \end{aligned}$$

where Eq. (7) has been used; and

$$< \overline{\det}\,(123),\ H\,\overline{\det}\,(1k\ell) > = < \overline{\det}\,(23),\ g_{12}\ \overline{\det}\,(k\ell) > \qquad (13)$$

and similarly for the rest of Eq. (10). Here $g_{12} = r^{-1}_{12}$ and $\overline{\det} = (1/\sqrt{6})\det$ on the left and $\overline{\det} = (1/\sqrt{2})$ det on the right of Eqs. (12) and (13). Notice that the non-vanishing properties of Eqs. (12) which will prove useful is due to the choice of the core orbitals $\underline{1}$ and $\underline{2}$ as H. F. SCF solutions of Li^+ rather than Li. We should remark however that actually with alkali atoms the self-consistent field of the outer electron has usually very little effect on the SCF wave functions of the core electrons and therefore the set of orbitals we have chosen are frequently employed in Hartree-Fock calculations on alkali-like configurations.[1,22]

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[22] See for example:

D. R. Hartree and W. Hartree, Proc. Cambridge Phil. Soc., 34, 550 (1938).

Equations (9) through (13) allow the separation of the second order energy in Eq. (6) into correlation energies of pairs of electrons. Of course it is a general result that whenever orthonormal functions are used and overlap and exchange effects are neglected, second order energies come out "pair-wise additive"[7] as in intermolecular "dispersion" forces. Three-body and higher correlations appear in higher orders of perturbation. However, we shall see shortly that here, Pauli Exclusion Principle already introduces some many-body correlations even in the second-order. The first order energy in Eq. (6) can be written as the energy of the ion core in the field of the bare nucleus and the energy of the outer electron in the SCF field of the ion core. For the ground state:

$$H_{oo} = < \overline{\det}\,(123),\ \Big(\sum_{i=1}^{3} h_i^{\circ} + \sum_{i>j}^{3} g_{ij} \Big)\ \overline{\det}\,(123) >$$

$$= \epsilon^{\circ}_{core}\,(12) + < 3,\ h^{eff}_{core}\ 3 > \qquad (14)$$

where $\epsilon^{\circ}_{core}\,(12) = 2 < 1s,\ h_1^{\circ}\ 1s > + < 1s\ 1s,\ g_{12}\ 1s\ 1s >$.

With the systematic classification of the virtual transitions in Eqs. (9) and (10), $E_o^{(2)}$ in Eq. (6) can be broken down into the following terms depending on which initial orbitals are involved:

$$E_o^{(2)}(123) = E_o^{(2)}\,(12) + E_o^{(2)}\,(23) + E_o^{(2)}\,(13)\ , \qquad (15)$$

where again numbers in parentheses label the orbitals, and not the electrons; and

$$-E_o^{(2)}(12) = \sum_{k > m > 3} \frac{< \overline{\det}(12),\ g_{12}\ \overline{\det}(m\ k) >^2}{\Delta(1,2,3 \longrightarrow m,\ k,\ 3)} \tag{16a}$$

$$-E_o^{(2)}(23) = \sum_{k > 3} \frac{< \overline{\det}(23),\ g_{12}\ \overline{\det}(k\ 3) >^2}{\Delta(1,\ 2,\ 3 \longrightarrow 1,\ k,\ 3)} \tag{17a}$$

$$+ \sum_{\ell > k > 3} \frac{< \overline{\det}(23),\ g_{12}\ \overline{\det}(k\ \ell) >^2}{\Delta(1,\ 2,\ 3 \longrightarrow 1,\ k,\ \ell)}$$

$$-E_o^{(2)}(13) = \sum_{m > 3} \frac{< \overline{\det}(13),\ g_{12}\ \overline{\det}(m\ 3) >^2}{\Delta(1,\ 2,\ 3 \longrightarrow m,\ 2,\ 3)} \tag{18a}$$

$$+ \sum_{\ell > m > 3} \frac{< \overline{\det}(13),\ g_{12}\ \overline{\det}(m\ \ell) >^2}{\Delta(1,\ 2,\ 3 \longrightarrow m,\ 2,\ \ell)}$$

The Δ's in the denominators are the energies of the respective virtual transitions and are given from Eq. (6) by:

$$\begin{aligned} \Delta(1,\ 2,\ 3 \longrightarrow m,\ k,\ \ell) = \ & < \overline{\det}(mk\ell),\ H\ \overline{\det}(mk\ell) > \\ & - < \overline{\det}(123),\ H\ \overline{\det}(123) > . \end{aligned} \tag{19}$$

In particular, when m is odd and k is even:

$$\Delta\,(1,2,3 \longrightarrow m,k,3) = \Delta h^{\circ}\,(1 \longrightarrow m) + \Delta h^{\circ}\,(2 \longrightarrow k) + (J_{mk} - J_{12}) + (J_{k3} - J_{23}) + (J - K)_{m3} - (J - K)_{13} \qquad (16b)$$

$$\Delta\,(1,2,3 \longrightarrow 1,k,3) = \Delta h^{\circ}\,(2 \longrightarrow k) + (J_{k1} - J_{21}) + (J_{k3} - J_{23}) \qquad (17b)$$

$$\Delta\,(1,2,3 \longrightarrow 1,k,\ ) = \Delta h^{\circ}\,(2 \longrightarrow k) + \Delta h^{\circ}\,(3 \longrightarrow \ell) + (J_{k1} - J_{21}) + (J_{k1} - J_{23}) + (J - K)_{\ell 1} - (J - K)_{31} \qquad (17c)$$

and similarly for Eq. (18a). J's and K's are the usual coulomb and exchange integrals

$$J_{rs} = \langle r\ s,\ g_{12}\ r\ s \rangle\ ;\ K_{rs} = \langle r\ s,\ g_{12}\ s\ r \rangle$$

and $\Delta h^{\circ}\,(r \longrightarrow s) = \langle s,\ h^{\circ}\ s \rangle - \langle r,\ h^{\circ}\ r \rangle$. The numerical evaluation of $E^{(2)}$ for any one case is a lengthy procedure because large contributions to such sums are to be expected[2] from the continuum (or from what would take the place of the continuum) part of the basis set $\{ k \}$. Our object here instead is to investigate semi-quantitatively various physical aspects of Eqs. (16a) to (18a) and their variation with the different actual excited states of the "series" electron.

The first part, Eq. (16a) corresponds to the correlation energy of the ion-core, $(1s_\alpha 1s_\beta)$ as it exists in the neutral atom. The effect of the "outer electron on this electron through the exclusion principle will be taken up later in Section III. Equations (17a) and (18a) give the correlation energy between an electron occupying 3, i.e. $2s_\alpha$ and those in 1 (i.e., $1s_\alpha$) and 2 (i.e. $1s_\beta$) respectively. The first terms on the right hand sides of Eqs. (17a) and (18a) represent the inner electrons in 1 and 2 making transitions in the average field of the orbital 3. The second terms of these equations give the correlation energy resulting from one core electron at a time making transitions simultaneously with the outer electron. At this point it should be emphasized that above we have referred to the entire core-"series" electron (or sigma-pi in organic molecules) correlation effects, i.e., the totality of the Eqs. (17a) or (18a), by the historical name of "core polarization," a name which has its origin in the adiabatic method, Eq. (1), and describes the polarization of the core by the instantaneous position of the electronic charge. The term "polarization" however is also used with reference to the virtual excitations caused in the core by the average electric field of the outer orbital, i.e. the first terms of Eqs. (17a), (18a).[10,23] The

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[23] O. Sinanoglu and K. S. Pitzer, J. Chem. Phys. (in press), (April 1960).

"polarization" effect in this more restricted sense is small, e.g. in Li, due to the spherical symmetry of (2s). In this more precise terminology the double excitations constitute the "dispersion" energy as in the intermolecular case.[10]

The sums in Eqs. (16a) to (18a) can be put into approximate but closed forms which are physically interesting by taking out the energy denominators as "mean excitation energies" in each case. This type of approximation is usually made for instance in the theory of intermolecular forces.[6,8,23] In the first parts of Eqs. (17a) and (18a), Δ's consist of excitations of single core electrons at a time, and hence are of the order of the ionization potential of Li^+, $(I_{Li}+)$, i.e.

$$\overline{\Delta\,(1,2,3 \longrightarrow 1,k,3)}^{\,k} \approx \overline{\Delta\,(1,2,3 \longrightarrow m,2,3)}^{\,m} = \bar{\delta}_c \approx I_{(Li^+)} \qquad (19)$$

where bars denote averages. The second "dispersion" parts of Eqs. (17a) and (18a) involve a similar single core excitation, but in addition virtual transitions of the outer electron in the field of the already excited core (See Eq. (17c)). Thus to define a "mean excitation energy" for the outer electron, an averaging over both k and ℓ in Eq. (17c) is necessary:

$$\overline{\Delta\,(1,2,3 \longrightarrow 1,k,\ell)}^{\,k,\ell} \approx \overline{\Delta h^{\circ}(2 \longrightarrow k) + (J_{k1} - J_{21})}^{\,k} \qquad (20)$$

$$+ \overline{\Delta h^{\circ}\,(3 \longrightarrow \ell) + (J - K)_{\ell 1} - (J - K)_{31} + (J_{k\ell} - J_{23})}^{\,k,\ell}$$

and

$$\overline{\Delta\,(1,2,3 \longrightarrow 1,k,\ell)}^{\,k,\ell} \approx \overline{\Delta\,(1,2,3 \longrightarrow m,2,\ell)}^{\,m,\ell} \equiv \bar{\delta}_C + \bar{\bar{\delta}}_V(3)$$

$$\approx I_{(Li^+)} + I_{(Li)} \qquad (21)$$

where $\bar{\bar{\delta}}_V(3)$ refers to the "mean excitation energy" of the valence, i.e. "series" electron initially occupying orbital 3. For our purposes only very rough ideas of the magnitudes of $\underline{\delta}$'s are necessary. Their use as semi-empirical parameters will be discussed later on. $\bar{\bar{\delta}}_V$ represents a small fraction of $\bar{\delta}_C$; moreover, the single excitation terms in Eqs. (17a) and (17b) are small as mentioned earlier. Thus neglecting the absence of $\bar{\bar{\delta}}_V$ in Eq. (19) (compare Eq. (20)) all the energy denominators may be equated and Eqs. (17a) and (18a) combined into one "series" electron-core correlation energy. For the ground state of Li:

$$- E_{CV}^{(2)}(3) = - E_o^{(2)}\,(23) - E_o^{(2)}(13) \approx$$

$$(\bar{\delta}_C + \bar{\delta}_V(3))^{-1} \Big(\sum_{\ell > k \geqslant 3} < \overline{\det}\,(23),\, g_{12}\,\overline{\det}\,(k\ell) >^2 + \sum_{\ell > m \geqslant 3} < \overline{\det}\,(13),\, g_{12}\overline{\det}(m\ell)>^2\Big)$$

For convenience, so far we have considered only the ground state ($\overline{\det}(123)$) of the Li atom and in Eqs. (9) and (10) analyzed the various types of virtual transitions that are possible from this state. Since however one of our objectives is to examine the validity of deriving an effective potential for the outer electron, before giving closed expressions for the sums in Eq. (22), it is necessary to consider the excited states of Li, ($\overline{\det}(12n)$) where now the "series" electron occupies the orbital (n).

With a different state of Li the second order sum in Eq. (6) again involves the same complete set of "ordered configurations," except that whereas before, $\overline{\det}$ (123) had been excluded and singled out as the zero order wave function, now the sum includes this determinant but instead excludes $\overline{\det}$ (12n), the new zero order wave function. $E^{(2)}$ in Eq. (6), or in operator form

$$- E_N^{(2)} = < N, \left\{ H \sum_{M \neq N} M > (H_{NN} - H_{MM})^{-1} < M, H \right\} N > = < N, Q_N^{(2)} N > \qquad (23)$$

where N denotes $\overline{\det}$ (12n), can be put also in the form of an expectation value over the "series electron orbital n. Denoting

$$N = \overline{\det}\ (12n) = A \left\{ n\ u_c\ (12) \right\}$$

where $$u_c\ (12) = \frac{1}{\sqrt{2!}} \det \quad (12)$$

and A is the operator anti-symmetricing n with the two core electrons, we obtain:

$$- E_N^{(2)} = < n \left\{ u_c(12), A\ H \sum_{M \neq N} M > (H_{NN} - H_{MM})^{-1} < M, H\ A\ u_c\ (12) \right\} n >$$

$$= < n, t_{cn}^{(2)}\ n > \qquad (24)$$

The curly parentheses in the second term have been placed to indicate that integrations over the coordinates in $\underline{n}$ are to be performed last. As it stands the formal core-"series" electron interaction operator $\underline{t}_{cn}^{(2)}$ is far from being a potential energy for $\underline{n}$. First, the summation over N includes all double virtual excitations of the core orbitals, (12); thus the part corresponding to Eq. (16a), the correlation energy of the core itself, has not yet been separated. As we have mentioned earlier, this part actually depends on $\underline{n}$, due to the "exclusion" principle and it will be taken up later. In addition if an arbitrary one electron basis set were to be used, $t_{cn}^{(2)}$ would depend on which $\underline{N}$ had been excluded from the sum in Eq. (23) or (24). On the other hand with an SCF H.F. basis or the basis $\{k\}$ we have chosen above, this type of dependence is eliminated, because the "series" electron orbitals satisfy Eq. (11). Thus in $E_0^{(2)}$ single virtual excitations from $\overline{\det}$ (123), i.e. the first of the Eqs. (9), would include:

$$1,2,3 \longrightarrow 1,2,n$$

whereas in $E_N^{(2)}$, the same type of excitations from $\overline{\det}$ (12n) would exclude 1,2,n but include:

$$1,2,n \longrightarrow 1,2,3$$

But both of these virtual transitions have zero matrix elements by Eq. (11) and hence are without effect on $t_{cn}^{(2)}$. The rest of Eqs. (9) and (10) can be generalized to any state of Li, $\overline{\det}$ (12n), keeping in mind the ordering of configurations in Eq. (2) by $k > \ell > m$ ($m = 1$ to ∞). Some transitions that were single core transitions for one state become "core"-n double transitions for another state and vice versa, as for example in

$$1,2,3 \longrightarrow 1,5,3$$
$$1,2,n \longrightarrow 1,3,5 \qquad (n \neq 3,5) \;;$$

otherwise the <u>totality</u> of the virtual transitions involving either a single core orbital or a single core orbital and the outer one, <u>n</u>, are unchanged. Thus after making the same approximations in the energy denominators, the core-valence electron correlation energy in Eq. (22) can be written for any "series" state of Li as:

$$-E_{CV}^{(2)}(n) = -E_N^{(2)}(2n) - E_N^{(2)}(1n) \approx$$

$$[\,\bar{\delta}_C + \bar{\delta}_V(n)\,]^{-1} \Big(\sum_{\ell > k \geqslant 3} < \overline{\text{det}}\,(2n),\, g_{12}\, \overline{\text{det}}\,(kl) >^2 + \sum_{\ell > m \geqslant 3} < \overline{\text{det}}(1n), g_{12} \overline{\text{det}}(m\ell)>^2 \Big)$$

where <u>n</u> > 2. The independence of the indices in the above sums, from <u>n</u>, is the biggest advantage of the way the basis set $\{k\}$ was chosen previously. (See Eqs. (12) and (7).) If the orbitals 1,2,3 had been taken as the completely SCF solutions of Li, the first terms in Eqs. (17a) and (18a) would have vanished and both the core orbitals 1, 2 and the summing indices in Eq. (25) would have been made to depend on the particular outer orbital.

We can now anticipate putting the sums appearing in Eq. (24) into closed forms and hope to obtain the desired potential (independent of *n*) were it not for the appearance of $\bar{\delta}_v(n)$ in the denominator. $\bar{\delta}_v(n)$ as in Eqs. (21) and (22) represents the "mean *virtual* excitation" energy of the outer orbital *n*. For *n* > 3, in some terms such as

$$1,2,n \longrightarrow 1,3,5 \qquad (n > 3,5),$$

of the equations corresponding to Eqs. (17a) and (18a), $n \longrightarrow 5$ would actually be a "de-excitation" and make a negative contribution to $\bar{\delta}_v(n)$. However, there are only a few such terms for low lying *n*, and the weight of any one term to the sum, e.g. in Eq. (17a) is small. As mentioned earlier, $\bar{\delta}_v(n)$ represents a small fraction of $\bar{\delta}_c$, so that it can either be neglected in comparison with $\bar{\delta}_c$ or replaced by a reasonable average[17], δ_s, for the few states $\overline{\det}$ (12n) of interest. Since $\delta_v(n)$ is small, the errors made by replacing it by δ_s will be even smaller. Assuming for the moment that the sums could be put in the suitable form, the requirement $(\bar{\delta}_v(n)/\bar{\delta}_c) < 1$ is necessary if any "core-polarization" potential derived from Eq. (25) is to be independent of *n*. Notice that this requirement is somewhat similar to the necessity of having the outer electron move slowly compared to the core electrons in the adiabatic approximation, except that here it does not enter in a fundamental way.

The summations in Eq. (25) can now be carried out. Since the core $(1s_\alpha 1s_\beta)$ is a closed shell it is necessary to discuss only those *n* that have either all *α* or all *β* spin. Take all *n* to be odd, i.e. with spin *α*, and in Eq. (25) consider first the pair involving opposite spins, i.e.

$\overline{\text{det}}\ (2n)$. Then:

$$\sum_{\ell > k \geqslant 3} < \overline{\text{det}}\ (2n),\ g_{12}\ \overline{\text{det}}\ (k\ell) >^2 = < \overline{\text{det}}\ (2n),\ g_{12}^2\ \overline{\text{det}}\ (2n) > \tag{26}$$

$$- \sum_{\substack{\ell > 2 \\ k = 2}} < \overline{\text{det}}\ (2n),\ g_{12}\ \overline{\text{det}}\ (2\ell) >^2 - \sum_{\substack{\ell > 1 \\ k = 1}} < \overline{\text{det}}\ (2n),\ g_{12}\ \overline{\text{det}}\ (1\ \ell) >^2$$

This follows from a matrix multiplication relation of the type:

$$\sum_{L = 1}^{\infty} < M,\ A\ L > < L,\ B\ N > = < M,\ (AB)\ N > \tag{27}$$

where $\underline{A}$ and $\underline{B}$ are operators acting on the space for which the set of orthonormal vectors $\left\{ L \right\} = 1, 2, 3, \ldots \infty$ form a complete basis. In Eq. (26) the set of all normalized two electron determinants corresponding to the ordered configurations $\ell > k \geqslant 1$, as in Eq. (2), form a complete orthonormal basis for the space of two electron coordinates (including spin) on which g_{12} acts. The spins of 2 and n being opposed, the determinantal matrix elements on the right hand side of Eq. (26) reduce to the direct integrals only; e.g. for the ground state of Li:

$$< \overline{\text{det}}\ (23),\ g_{12}^2\ \overline{\text{det}}\ (23) > = < 1s\ 2s,\ g_{12}^2\ 1s\ 2s > \tag{28}$$

Similarly

$$\sum_{\ell > 2} < \overline{\det}\,(2n),\ g_{12}\ \overline{\det}\,(2\ell)\ >^2 = \sum_{\substack{\ell > 2 \\ (\ell\, =\, \text{odd})}} < 2n,\ g_{12}\ 2\ell >^2 \qquad (29)$$

where to conserve spin, $\underline{\ell}$ must have spin $\underline{\alpha}$, i.e. be odd. The last sum can be evaluated too by carrying out the integrations in each matrix element over one set of the electron coordinates and thus obtaining a function $W_{2,2}$ of the other electron coordinates only; i.e.

$$< 2n,\ g_{12}\ 2\ \ell >^2 = < n,\ W_{2,2}\ \ell >^2 \qquad (30)$$

where $W_{2,2} = \int |\ 1s\ (1)\ |^2\ \ r_{12}^{-1}\ d\ \ \tau_1$

Then, making use of Eq. (27) we get (31)

$$\sum_{\substack{\ell > 2 \\ (\ell\, =\, \text{odd})}} < 2n,\ g_{12}\ 2\ell >^2 = \sum_{\substack{\ell > 2 \\ (\ell\, =\, \text{odd})}} < n,\ W_{2,2}\ \ell >^2 = <\ n,\ (W_{2,2})^2\ n > - < n, W_{2,2}\ 1 >^2$$

$$- < n,\ W_{2,2}\ 1 >^2\ , \qquad (31)$$

since $\ell = 1, 3, 5, \ldots$ odd $\ldots \infty$ form a complete one electron basis set and $W_{2,2}$ of Eq. (30) is a function of the coordinates of a single electron. In the same way, in Eq. (26)

$$\sum_{\ell > 1} < \overline{\det}\,(2n),\ g_{12}\ \overline{\det}\,(1\ \ell) >^2\ = \sum_{\substack{\ell > 1\\ (\ell = \text{even})}} < 2n,\ g_{12}\ \ell\, 1 >^2$$

$$= \sum_{\substack{\ell > 1\\ (\ell = \text{even})}} < 2,\ W_{n,1}\ \ell >^2\ = < 2,\ (W_{n,1})^2\ 2 > \tag{32}$$

since now to conserve spin $\underline{\ell}$ must be even (spin (β)) and $\underline{\ell} = 2,4,6,\ \ldots$ even$\ldots\infty$ form a complete basis set for functions of the spatial coordinates of one electron.

Similarly for the parallel spin pair (1n) in Eq. (25) the use of Eq. (27) leads to

$$\sum_{\ell > m \geqslant 3} < \overline{\det}\,(1n),\ g_{12}\ \overline{\det}\,(m\ell) >^2\ = < \overline{\det}\,(1n),\ g_{12}^2\ \overline{\det}\,(1n) > \tag{33}$$

$$- \sum_{\ell > 2} < \overline{\det}\,(1n),\ g_{12}\ \overline{\det}\,(2\ell) >^2 - \sum_{\ell > 1} < \overline{\det}\,(1n),\ g_{12}\ \overline{\det}\,(1\ \ell) >^2 .$$

Now both of the spin orbitals $\underline{1}$ and $\underline{n}$ have spin $\underline{\alpha}$, so that

$$< \overline{\det}\,(1n),\ g_{12}^2\ \overline{\det}\,(1n) > = < 1n,\ g_{12}^2\ 1n > - < 1n,\ g_{12}^2\ n1 > \tag{34}$$

Also, since $\underline{2}$ has spin β:

$$\sum_{\ell > 2} < \overline{\det}\,(1n),\ g_{12}\ \overline{\det}\,(2\ \ell) >^2 = 0 \tag{35}$$

The last term of Eq. (33):

$$\sum_{\ell > 1} < \overline{\det}\,(1n),\ g_{12}\ \overline{\det}\,(1\ \ell) >^2 = \sum_{\substack{\ell > 1 \\ (\ell = \text{odd})}} [\ < 1n,\ g_{12}\ 1\ \ell > - < 1n, g_{12} 1\ \ell >\ ]^2 \tag{36}$$

$$= \sum_{\substack{\ell > 1 \\ (\text{odd})}} < n,\ W_{1,1}\ \ell >^2 + \sum_{\substack{\ell > 1 \\ (\text{odd})}} < 1,\ W_{n,1}\ \ell >^2 - 2 \sum_{\substack{\ell > 1 \\ (\text{odd})}} < n,\ W_{1,1} \ell > < \ell, (W_{n,1}) 1$$

defining the one electron functions as in Eq. (30). Then using Eq. (27) in each term of the last expression,

$$\sum_{\ell > 1} < \overline{\det}\,(1n),\ g_{12}\ \overline{\det}\,(1\ \ell) >^2 = < n,\ (W_{1,1})^2\ n > + < 1, (W_{n,1})^2\ 1 >$$

$$- 2 < n,\ (W_{1,1})(W_{n,1})\ 1 > \tag{37}$$

and, from Eq. (33):

$$\sum_{\ell > m \geqslant 3} < \overline{\det}\,(1n),\ g_{12}\ \overline{\det}\,(m \ell) >^2 = < 1n,\ g_{12}^2\ 1n > - < 1n,\ g_{12}^2\ n1 >$$

$$- < n,\ (W_{1,1})^2\ n > - < 1,\ (W_{n,1})^2\ 1 > + 2 < n, (W_{1,1})\ (W_{n,1})\ 1 >. \tag{38}$$

Before going into the correlation energy of the core itself and deriving expressions for it similar to those given above, let us examine the meaning of the various terms in the results for $E_{CV}^{(2)}(n)$, Eq. (25). The major part of the core-valence electron correlation energy is due to pair with opposing spins, i.e. $E_N^{(2)}(2n)$, since the other $\underline{\alpha}\,\underline{\alpha}$ pair electrons are already kept apart by the Pauli exclusion principle. By Eqs. (26) and (29) through (32), the $\alpha\beta$ - pair energy for some state $\overline{\text{det}}\,(12n)$ of Li is given by:

$$- E_N^{(2)}(2n) \approx (\bar{\delta}_C + \delta_S)^{-1} [< 2n, g_{12}^2\, 2n > - < n, (W_{2,2})^2\, n > + < n, (W_{2,2})\, 1 >^2 - < 2, (W_{n,1})^2\, 2 >] . \tag{39}$$

or for the ground state of Li with n = 3, replacing 1 = $(1s)\alpha$, 2 = $(1s)_\beta$ and 3 = $(2s)_\alpha$

$$- E_o^{(2)}((1s)_\beta\, (2s)_\alpha) \approx (\bar{\delta}_C + \delta_S)^{-1} (< (2s), F_{(1s)}\, (2s) > - R_{(1s_\beta)(2s_\alpha)}) \tag{40}$$

where we have defined

$$< (2s), F_{(1s)}\, (2s) > \equiv < (2s)(1s), g_{12}^2\, (2s)(1s) > - < (2s), W_{(1s)(1s)} (2s) > \tag{41a}$$

$$\text{and} \quad R_{(1s_\beta)(1s_\alpha)} \equiv < (1s), W_{(2s),(1s)}^2 (1s) > - < 1s\, 2s, g_{12}\, 1s\, 1s >^2 . \tag{41b}$$

Clearly $F_{(1s)}$ represents a true potential acting on the outer electron, and depends solely on the core orbital (1s); it is given by

$$\boxed{F_{(1s)}(\underset{\sim}{r}_2)} = \left(\int |\, 1s(\underset{\sim}{r}_1)\,|^2 \frac{1}{|\underset{\sim}{r}_2 - \underset{\sim}{r}_1|^2}\, d\tau_1 \right) - \left(\int |\, 1s(\underset{\sim}{r}_1)\,|^2 \frac{1}{|\underset{\sim}{r}_2 - \underset{\sim}{r}_1|}\, d\tau_1 \right)^2 \tag{42}$$

where $\underset{\sim}{r}_2$ and $\underset{\sim}{r}_1$ are the position coordinates in (2s) and (1s) respectively, and the potential acting at $\underset{\sim}{r}_2$ is obtained by integration over all $\underset{\sim}{r}_1$. $F_{(1s)}(\underset{\sim}{r}_2)$ in Eq. (42) can be identically written as:

$$F_{(1s)}(\underset{\sim}{r}_2) = \left< (1s)_1 \left[\frac{1}{r_{12}^2} - \left< (1s)_1 \frac{1}{r_{12}} (1s) \right>_1^2 \right] (1s) \right>_1 =$$

$$\left< (1s)_1 \left[\frac{1}{r_{12}} - \left< (1s)_1 \frac{1}{r_{12}} (1s) \right>_1 \right]^2 (1s) \right>_1$$

$$= \overline{\left(g_{12} - \overline{g_{12}}^{(1s)} \right)^2}^{(1s)}$$

where $< \ >_1$ means that all integrations in Eq. (43) are over the same coordinates $\underset{\sim}{r}_1$ as in Eq. (42). In the last term we have denoted the quantum mechanical averages of the "source point" $\underset{\sim}{r}_1$ over (1s) with bars. It will be noticed that $(g_{12} - \overline{g_{12}}^{1s})$ simply represents the "instantaneous" (in the virtual sense) deviation of the electrostatic potential, produced at the point $\underset{\sim}{r}_2$ by the electronic charge at $\underset{\sim}{r}_1$, from the orbital average (i.e. the expectation value over 1s $(\underset{\sim}{r}_1)$) potential of the electron $(\underset{\sim}{r}_1)$ produced at $\underset{\sim}{r}_2$. Thus as we had done in the theory of Van der Waals' interactions between molecules and solid surfaces,[23] $F_{(1s)}(\underset{\sim}{r}_2) / \bar{\delta}_C$ may be called the "fluctuation" potential, since $F_{(1s)}(\underset{\sim}{r}_2)$ is simply the "mean" square fluctuation of the coulombic potential of the orbital (1s) at the point $\underset{\sim}{r}_2$.

In Eq. (40), there still exists a remainder term $R_{(1s)_\beta (2s)_\alpha}$ which cannot be put in the form of an expectation value of a potential. A close examination of the Eqs. (26) through (32) leading to Eq. (40) shows that $R_{(1s)_\beta (2s)_\alpha}$ arises because the closed inner shell $(1s_\alpha\ 1s_\beta)$ of Li prevents the outer electron occupying $2s_\alpha$ from making virtual transitions to these already occupied inner levels. This is one of the "exclusion" effects that were mentioned in the introduction and represents the "non-pairwise additive" effect of $(1s_\alpha)$ on the pair $(1s_\beta\ 2s_\alpha)$. $R_{(1s_\beta)(n)}$ has been neglected in the previous treatments of "core-polarization" for "non-penetrating" orbitals.[13,14,16,17] However especially for the ground state its magnitude requires examination (See Section IV).

Likewise, the correlation energy of the $\alpha\,\alpha$ pair $(1s_\alpha\ 2s_\alpha)$ of the ground state of Li in Eq. (25) is given from Eqs. (38), (40) and (41) by:

$$-E_o^{(2)}(1s_\alpha\ 2s_\alpha) \simeq (\bar{\delta}_C + \delta_S)^{-1} [< (2s), F_{(1s)}(2s) > - < (2s), \overset{ex.}{F}_{(1s)}(2s) > - \overset{ex.}{R}_{1s_\alpha 2s_\alpha} \tag{44}$$

where:

$$< (2s), \overset{ex.}{F}_{(1s)}(2s) > = < 2s\ 1s, g_{12}^2\ 1s\ 2s > - < 2s, (W_{1s,1s})(W_{1s,2s})\ 1s > \tag{45a}$$

and:

$$R^{ex.}_{1s_\alpha 2s_\alpha} \equiv \langle 1s, (W_{2s,1s})^2 \, 1s \rangle - \langle 2s, (W_{1s,1s})(W_{1s,2s}) \, 1s \rangle \qquad (45b)$$

Comparison of the Eqs. (38) and (44) with (39) and (40) shows that $E_o^{(2)}$ $(1s_\alpha \, 2s_\alpha)$, in addition to the "fluctuation" potential of $E_o^{(2)}$ $(1s_\beta 2s_\alpha)$ contains $F^{ex.}_{(1s)} \; / \; (\bar{\delta}_C + \delta_S)$ or what may be called the "exchange fluctuation potential." Note that the latter is a "potential" only in exactly the same sense^2 as the exchange part of the Hartree-Fock field (See Eq. (8)) is. The "exclusion" term in Eq. (45b) is similar to that in Eq. (41b). Combining Eqs. (6), (7), (14), (15), (40) and (44) the total energy of Li in any state $N = \overline{\det}$ (12n) is obtained:

$$E_N \, (12n) \cong H_{NN} + E_N^{(2)} \cong \epsilon^o_{core} \, (12) + \langle n, h^{eff}_{core} \; n \rangle + E_N^{(2)} \, (12) + \langle n, U_f \, n \rangle + Q_n \qquad (46)$$

$$= E_N(core) + \langle n, (h^{eff}_{core} + U_f) \, n \rangle + Q_n$$

where $$U_f = \frac{2F_{(1s)} - F^{ex.}_{(1s)}}{\bar{\delta}_C + \delta_S} \qquad \text{and} \qquad Q_n = \frac{R_{1s_\beta n} + R^{ex}_{1s_\alpha n}}{\bar{\delta}_C + \delta_S}$$

E_N (core) contains the H. F. energy (Eq. (14)) of the free ion Li$^+$, but in addition the correlation energy $E_N^{(2)}$ (12) (given for the ground state by Eq. (16a)) which refers not to free Li$^+$ but to the core as it exists in the state $\underline{N}$ of Li. The dependence of $E_N^{(2)}$ (12) on the outer orbital $\underline{n}$ through the "exclusion" principle will be discussed in Section III. Q_n is the rest of the "exclusion" effects. It depends on the exchange charge density of $\underline{n}$ with ($\underline{1s}$) so that it will be small for excited states of Li, i.e. "non-penetrating" $\underline{n}$. $\underline{U_f}$ is the desired correlation (fluctuation) potential. With a larger atom similar results can easily be written down. In general there will be a contribution from each electron of the core to $\underline{U_f}$ and Q_n. After estimating the "exclusion" effects, U_f can be determined semi-empirically (see e.g. Douglas[3]) for instance by leaving $(\bar{\delta}_C + \delta_S)$ as a parameter. Aside from the "exclusion" effects, Eq. (46) has the variational form for the outer electron with an effective "core-Hamiltonian." It is important to realize however that in this form $\underline{n}$ cannot be varied to improve the energy even when $Q_n \sim 0$ and E_N (core) $\sim$ constant, because the result was derived for a specific choice of orbitals for $\underline{n}$, namely those satisfying the H. F. condition, Eq. (11). With any other choice, the single virtual transitions of $\underline{n}$ as in Eq. (9) would lead to non-vanishing matrix elements and make a new contribution to Eq. (46). This point brings out the connection between the present treatment and the recent nuclear many-body theory.[11,24] In fact Eq. (46) corresponds to a starting approximation

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[24] Brueckner, Levinson and Mahmond, Phys. Rev., 95, 217 (1954); for later references see e.g.: H. Yoshizumi, in Advances in Chem. Phys., Vol. II., Interscience Publishers, New York, 1959; pp. 323 ff.

of that theory with neglect of higher order correlations (Section V) as can be seen for instance from the work of Bethe[25] and Rodberg.[26]

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[25] H. A. Bethe, Phys. Rev. **103**, 1353 (1956).

[26] L. S. Rodberg, Ann. Phys. **2**, 199 (1957).

Improved choices for n can be made and perhaps restrictions as in Eq. (11) removed by going to higher orders of perturbation, but such generalizations will be deferred to a future date.

III. "Exclusion" Effect of an Outer Electron on the Core Energy

The dependence of the core correlation energy $E_N^{(2)}$ (12) in Eq. (46) on the outer orbital n in Li can be examined by a careful classification of all the "ordered configurations" entering Eq. (6) and generalization of Eq. (16a) to any n. In Eq. (10) some of the configurations that corresponded to double virtual transitions from the core ($1s_\alpha\ 1s_\beta$) when n was 3 (i.e. $2s_\alpha$) become triple transitions from another initial state $\overline{\text{det}}$ (12n) with $n > 3$, and vice versa. Including all such configurations in $E^{(2)}$ one obtains the expected result that:

$$-E_N^{(2)}(12) = \sum_{\substack{k > m \geqslant 3 \\ (k,m \neq n)}} \frac{< \overline{\text{det}}\,(12),\ g_{12}\ \overline{\text{det}}\,(mk) >^2}{\Delta\,(1,2,n \longrightarrow m,k,n)} \quad ; \tag{47}$$

i.e. all the double core transitions $1,2 \longrightarrow m,k$ are missing when m or k is the already occupied orbital n. This may be compared with the second order energy of the free ion core Li^+ using the same one electron basis set $\{k\}$ that was defined previously for Li:

$$-E_{Li^+}^{(2)}(12) = \sum_{k > m > 2} \frac{< \overline{\text{det}}\,(12),\ g_{12}\ \overline{\text{det}}\,(mk) >^2}{\Delta\,(1,2 \longrightarrow m,k\ )} \tag{48}$$

The energy denominator in Eq. (47) differs from that in Eq. (48) by the presence of n (See Eq. (19)). Nevertheless a semi-quantitative estimate of the variation of $E_N^{(2)}$ (12) with n and its difference from the energy of Li^+ can be obtained by replacing both Δ's by one average, $\bar{\Delta}_{core} \sim (I_{Li^+} + I_{Li^{++}})$. Then comparing Eqs. (47) and (48):

$$E^{(2)}_{Li\ core}(n) \equiv E_N^{(2)}(12) \sim E^{(2)}_{Li^+}(12) + \frac{1}{\bar{\Delta}_{core}} \sum_{k>3}^{\infty} < \overline{det}\,(12),\ g_{12}\overline{det}(nk) >^2 \tag{49}$$

or using Eq. (27) as in Eq. (32):

$$E_N^{(2)}(12) \sim E^{(2)}_{Li^+} + \frac{1}{\bar{\Delta}_{core}} \Big[< (1s),\ (W_{(1s),n'})^2\,(1s) > \tag{50a}$$

$$- < (1s)(n'),\ g_{12}\,(1s)(1s) >^2 \Big] = E_{Li^+} + \frac{R_{core-n}}{\bar{\Delta}_{core}}$$

with n'α = n, and from Eq. (46):

$$E_N(core) \cong E_{Li^+} + \frac{1}{\bar{\Delta}_{core}} \Big[< (1s),\ (W_{1s,n'})^2\,(1s) > - < (1s)n',\ g_{12}\,(1s)(1s) >^2 \Big] \tag{50b}$$

The last term is the desired "exclusion" effect of n' on the core. With any larger system, the evaluation of all such "exclusion" effects is similarly possible from a classification of ordered configurations and use of Eq. (27) for summations.

IV. Magnitudes for the Ground State of Lithium

In Section II, Eq. (46) we have obtained an expression for the total energy of Li atom in any one of its "series" states. That derivation shows that aside from the "exclusion" effects, $\underline{U}_f$ is the desired "core-polarization" potential including exchange and it may be regarded as the mean square fluctuation of the Hartree-Fock potential of the core per unit of "mean excitation energy." $\underline{U}_f$ is not dependent on a multipole expansion of g_{12}. In the previous treatments[12-17] of "core-polarization" a) the "exclusion" effects, b) the exchange part of U_f $(F_{1s}^{ex.}/\bar{\delta}_C + \delta_S)$ has been neglected (see however Ludwig)[15] and c) after making a multipole expansion of g_{12}, as

$$g_{12} = \frac{1}{r_{12}} = \frac{1}{r_>} + \frac{r_<}{r_>^2} (\cos \omega) + \frac{r_<^2}{2r_>^3} (3 \cos^2 \quad - 1) + \dots \qquad (51)$$

mainly the dipole term (with estimates of quadrupole terms) has been considered and the first part $r_>^{-1}$ dropped. In Eq. (51) $r_>$ denotes the greater of the two distances $\underline{r}_1$ and $\underline{r}_2$, and $\underline{\omega}$ is the angle between the radius vectors of the two electrons. For highly excited states, i.e. with larger $\underline{n}$, assumptions $\underline{a}$ to $\underline{c}$ approach validity. For instance as the portion of the outer orbital that is inside the core becomes negligible, we get $r_> = r_2$ only, so that $r_>^{-1}$ part of g_{12} no longer contributes to U_f (See Eqs. (41) and (45)). For "penetrating" orbitals however such is not the case. To get an idea of the various neglected magnitudes we shall consider the ground state of Li for which the effects should be largest. We take for 2s the orthogonalized Slater orbital

$$2s^{o} = 1.0148\,(\delta_2{}^5/3\pi)^{1/2}\, r \exp(-\delta_2 r) - 0.1742\,(\delta_1{}^3/\pi)^{1/2} \exp(-\delta_1 r) \qquad (52a)$$

with $\delta_1 = 2.65$ and $\delta_2 = 0.65$, which sufficiently approximates the Hartree-Fock (*2s*) orbital of Fock and Petrashen,[24] and for 1s:

$$1s = (\delta_1{}^3/\pi)^{1/2} \exp(-\delta_1 r) \qquad (52b)$$

with $\delta_1 = 2.65$. The "exclusion" terms in Eqs. (41b), (45b) and (50b) involve g_{12} in the $\underline{W}$ integrals. These are like the usual atomic integrals[25] and upon substitution of Eq. (51) for $\underline{g}_{12}$, only the $\underline{r}_{>}^{-1}$ term contributes due to the spherical symmetry of *1s* and *2s*. The first parts of $\underline{F}_{(1s)}$ and $\underline{F}^{ex.}_{(1s)}$ in U_f on the other hand, contain $\underline{g}_{12}^{2}$ and such integrals can be more conveniently obtained by an expansion in terms of Gegenbauer polynomials,[26] $C_n^{(1)}$ (cos ω):

$$g_{12}^{2} = \frac{1}{r_{12}^{2}} = \frac{1}{r_{>}{}^{2}} \sum_{n=0}^{\infty} \left(\frac{r_<}{r_>} \right)^n C_n^{(1)} (\cos \omega) \qquad (53)$$

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[24] V. Fock and M. J. Petrashen, Physik Z. Sowjetunion, 8, 547 (1935).

[25] Condon and Shortley, *The Theory of Atomic Spectra*, (Cambridge University Press, 1957); p. 174

[26] For a quite detailed account of these polynomials, see e.g.: I. Prigogine, *et al.*, *Molecular Theory of Solutions* (North-Holland Publishing Co., Amsterdam 1957) p. 265.

These polynomials are analogous to the Legendre polynomials and have similar addition theorems. The first term of Eq. (53) is $\underline{r_>}^{-2}$, neglected previously[12-17] corresponding to assumption ($\underline{C}$); its contribution to Eq. (46) will be calculated here.

With the orbitals Eq. (52), the desired integrations can be performed analytically and yield: (54)

$$< 2\overset{o}{s}, (W_{1s,1s})^2\, 2s^o > = < 2s^o, \left(\int |1s\ (r_1)\ |^2\, r_>^{-1}\, d\ \tau_1 \right)^2 2s^o > = 0.16144\ (a.u.)^2$$

$$< 1s, (W_{2s^o,1s})^2\, 1s > = 0.018537\ (a.u.)^2$$

$$< 1s\ 2\overset{o}{s}, g_{12}\ 1s\ 1s >^2 = < 1s\ 2\overset{o}{s}, r_>^{-1}\ 1s\ 1s >^2 = 0.013855\ (a.u.)^2$$

$$< 2\overset{o}{s}, (W_{1s,1s})\, (W_{2\overset{o}{s},\ 1s})\ 1s > = 0.029806\ (a.u.)^2$$

$$< 2\overset{o}{s}, 1s, r_>^{-2}\ 2\overset{o}{s}\ 1s > = 0.17385\ (a.u.)^2$$

$$< 2\overset{o}{s}\ 1s, r_>^{-2}\ 1s\ 2\overset{o}{s} > = 0.053256\ (a.u.)^2$$

where 1 ($\underline{a}.\underline{u}$.) = 27.202 $\underline{ev}$. and e.g.

$$\frac{1}{4\pi} \int |1s(r_1)|^2\, r_>^{-2}\, d\tau_1 = \frac{1}{r_2{}^2} \int_0^{r_2} |\ 1s(r_1)|^2\, r_1{}^2\, dr_1 + \int_{r_2}^{\infty} |1s(r_1)|^2\, dr_1 \qquad (55)$$

Substituting these results in Eqs. (41b), (45b) and (50b) and taking as estimates $\bar{\delta}_C + \delta_S \approx 3$ (a.u.) and $\bar{\Delta}_{core} \approx I_{Li^+} + I_{Li^{++}} = 7.24$ (a.u.) we obtain:

$$(\bar{\delta}_C + \delta_S)^{-1} R_{1s_\beta 2s_\alpha} = 0.04245 \text{ ev.} \qquad (56a)$$

$$(\bar{\delta}_C + \delta_S)^{-1} R_{1s_\alpha 2s_\alpha} = -0.1022 \text{ ev.} \qquad (56b)$$

$$(\bar{\Delta}_{core})^{-1} R_{core-2s_\alpha} = 0.0176 \text{ ev.} \qquad (56c)$$

and using only the first terms of g_{12} and g_{12}^2 from Eqs. (51) and (53) in Eqs. (40) and (44) and denoting the corresponding parts of $F_{(1s)}$ and $F_{(1s)}^{ex}$ by:

$$< \overset{o}{2s}, F_{r_>} \overset{o}{2s} > \equiv < \overset{o}{2s}\ 1s, r_>^{-2}\ \overset{o}{2s}\ 1s > - < \overset{o}{2s}, (W_{1s,1s})^2\ \overset{o}{2s} > \qquad (57)$$

$$< \overset{o}{2s}, F_{r_>}^{ex} \overset{o}{2s} > \equiv < \overset{o}{2s}\ 1s, r_>^{-2}\ 1s\ \overset{o}{2s} > - < \overset{o}{2s}, (W_{1s,1s})(W_{1s,2s})\ 1s >$$

we get:

$$(\bar{\delta}_C + \delta_S)^{-1} < \overset{o}{2s}, F_{r_>} \overset{o}{2s} > = 0.1125 \text{ ev.} \qquad (58a)$$

$$(\bar{\delta}_C + \delta_S)^{-1} < \overset{o}{2s}, F_{r_>}^{ex} \overset{o}{2s} > = 0.2126 \text{ ev.} \qquad (58b)$$

Essentially the same values are obtained by the use of $\delta_1 = 2.70$ instead of 2.65 in $\underline{\overset{o}{2s}}$ and $\underline{1s}$ so that the results are not very sensitive to the specific choice of the orbitals in Eqs. (52).

Most of the "penetration" effects of $\underline{2s}$ are included in Eqs. (56), (57) and (58) as can be seen for instance from the fact that only $r_>^{-1}$ contributes to the "exclusion" terms. Callaway[13] has obtained a "core-polarization" potential in Li using only the dipole part of g_{12}, equivalent to taking the second term of Eq. (53) in $F_{(1s)}$ and neglecting $F^{ex}_{(1s)}$. He finds a contribution of 0.1 ev. to $< 2s, U_f\ 2s >$. Actually the results of Ludwig[15] suggest that the exchange term in the dipole part may be negligible. Thus by comparison several interesting conclusions follow from the Eqs. (56), (57) and (58). First, the "exclusion" effect of the outer orbital on the core correlation energy is only 0.0176 ev., hence quite negligible even for <u>2s</u>. Then in Eq. (50) we can take E_N (core) $\sim E_{Li^+}$. Secondly, the total contribution to the correlation energy of the $1s_\beta 2s_\alpha$ pair from the $r_>^{-1}$ terms is $(\bar{\delta}_C + \delta_S)^{-1} (< \overset{o}{2s}, F_{r_>}\ \overset{o}{2s} > - R_{1s_\beta\, 2s_\alpha})$ or 0.1125 - 0.0425 = 0.0702 ev. and is comparable to the total dipole contribution[13] 0.1 ev. from both of the core electrons. The <u>average</u> or "polarization" (in the restricted sense[10,23] of the word) effect of the <u>orbital</u> <u>2s</u>, also appears only in the $\underline{r_>}^{-1}$ part of $\underline{g}_{12}$ due to spherical symmetry. This effect, as it was mentioned earlier is not strictly a "correlation" effect since it results in converting the Li^+ H.F. SCF orbitals to the completely H.F. SCF orbitals in Li. The term, $\underline{F}_{r_>^{-1}}$, we have calculated above however, corresponds to the "fluctuation" of $\underline{r_>}^{-1}$, i.e. $< \underline{r_>}^{-2} - < \underline{r_>}^{-1} >_1^2 >_1$, hence to the inclusion of the "dispersion" effect. It is much larger than the strictly "polarization" energy. Thirdly, combining all the $\underline{r_>}$ or "penetration" terms for the $\underline{1s_\alpha 2s_\alpha}$ pair we find that

$$(\underline{\bar{\delta}}_C + \underline{\delta}_S)^{-1} (< \overset{o}{2s}, F_{r_>}\ \overset{o}{2s} > - < \overset{o}{2s}, F^{ex}_{r_>}\ \overset{o}{2s} > - R^{ex}_{1s_\alpha 2s_\alpha}) = 0.00208 \text{ ev.}$$

an entirely negligible value. Thus the "Fermi hole" is very effective in keeping the electrons of the $\underline{\alpha}\,\underline{\alpha}$ pair apart and not necessitating a "Coulomb hole." Hence to obtain the over-all "core-polarization" potential we need to add the $r_>^{-1}$ terms only for the $1s_\beta 2s_\alpha$ pair. Then neglecting exchange in dipole and higher order terms, $\underline{U}_f$ in Li may be taken as

$$U_f \sim (\bar{\delta}_C + \delta_S)^{-1} [\, F_{r_>} + 2(F_{(1s)} - F_{r_>})\,] \qquad (59)$$

V. Molecules

The treatment that was given in previous sections and demonstrated in detail for the case of Li atom, can be applied to any N-electron system whose zero-order wave function is a single Slater determinant of H. F. orbitals. Thus the second-order energy of most molecules can be separated into "pair correlations" and non-pairwise additive "exclusion" effects by taking the H. F. SCF molecular orbitals (MO) as the one electron basis set $\left\{ \underline{k} \right\}$. These orbitals are for instance obtainable by Roothaan's procedure.[27] Again each energy component can be obtained in closed form, by taking out the denominators as "mean excitation energies" for each electron pair. Although rather crude, this procedure has the advantage that the various energy components are then obtainable using only the same H. F. orbitals as in the initial single determinant. Contrary to the use of an average energy denominator for the over-all second order energy[28] here each "mean excitation energy" has a more physical basis and can be estimated or left as a semi-empirical parameter especially for those electron groups that are relatively unchanged in going from an atom or molecule to another. More directly, two specific applications

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[27] C. C. J. Roothaan, Revs. Mod. Phys., 23, 69 (1951).

[28] P. Kessler, Compt. Rendu 242, 350 (1955).

are suggested by this approach as mentioned in the introduction. Both of them may be demonstrated with reference to the Li_2 molecule for convenience. In this molecule the first four MO's of the one electron basis $\left\{ \underline{k} \right\}$ are $(\sigma_g \underline{1s})^2 (\sigma_u \underline{1s})^2$. When the atomic orbitals (AO) that make up such inner shells do not overlap appreciably as in Li_2, we can perform a unitary transformation on the $(\underline{\sigma}_g, \underline{1s})^2(\underline{\sigma}_u \underline{1s})^2$ part of the basis only and convert the MO determinant $\overline{\text{det}}\ [\ (\underline{\sigma}_g \underline{1s})^2 (\underline{\sigma}_u \underline{1s})^2\ ]$ into the ion core description $\overline{\text{det}}\ [\ (\underline{1s}_a)^2 (\underline{1s}_b)^2\ ]$, i.e. K_aK_b, where $\underline{a}$ and $\underline{b}$ refer to the two nuclei, assuming that admixture of other AO's is negligible. Then taking $(\underline{1s}_a)^2 (\underline{1s}_b)^2$ equivalently, as the first four spin-orbitals of $\left\{ \underline{k} \right\}$ with the rest of the MO's unchanged, a classification of all "ordered configurations" as in Eqs. (9) and (10) into various types of virtual transitions leads to a separation of the correlation energy as in Eqs. (16) to (18). We get the total energy of the molecule separated as in Eq. (46) into the energy of two free Li^+'s (including their individual $E^{(2)}$'s), the energy of the two H. F. MO valence electrons $(\sigma_g \underline{2s})^2$, each in the field of both cores including the core "fluctuation potentials" (the effective "core-hamiltonian" from one Li^+ is $(h^{eff}_{core} + \underline{U}_f)_a)$, the energy of the two valence electrons (as in H_2), $E^{(2)}_{(\sigma_g 2s)^2}$, and finally the correlation energy between the two cores $\underline{K}_a$ and $\underline{K}_b$. There are also the "exclusion" terms associated with each of these components.

The first application concerns the "core polarization" energy between a valence electron and the ion-cores. When these cores can be assumed quite unchanged, the expectation value of the potential, $\underline{U}_f$ determined from e.g. Eq. (59) in conjunction with the "series" levels of the atom, may be calculated over the ground or an excited state valence MO in the molecule. Thus for instance the calculation of the contribution of "core polarization" to the already small binding energy of a diatomic alkali molecule is possible. Callaway[13] has made such calculations on alkali metals and found appreciable values even with just the dipole part (see Section IV) of $\underline{U}_f$. In this type of application the change in the "exclusion" energy $(\bar{\delta}_C + \delta_S)\, R_{1s_\beta n_\alpha}$ (Eq. 56a) also needs to be estimated.

The second application, although a small effect in the case of Li_2, concerns the correlation energy between the two cores, $\underline{K}_a$ and $\underline{K}_b$ themselves. This energy which can be written in the "fluctuation" form similar to Eq. (41) and including the exchange part, is just the "dispersion" (plus "polarization") energy which on making a multipole expansion (or more conveniently "Gegenbauer" expansion[26] as in Eq. (53) but now for two centers) for g_{12}^2 and taking the second term would simply lead to London's formula.[6] Aside from not requiring such an expansion, the approach presented here now includes the exchange terms as well as the "exclusion" effects similar to that in Eq. (50), but with the appropriate orbitals. It is particularly important to recognize that the discussion given here does not require the two cores to occupy completely isolated spaces each with its own distinct basis set as in the case of London forces.[29] Starting from a complete set of MO's it has been necessary

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[29] See also: H. C. Longuet-Higgins, Proc. Roy. Soc. (Lond.) A235, 537 (1956)

to assume the non-overlapping of AO's only for the first four MO's, $(\sigma_g\ 1s)^2\ (\sigma_u\ 1s)^2$, to get into the K_aK_b description. In general such an assumption is much more plausible than requiring essentially the complete localization of the core electrons around different centers, each group with its own distinct eigenfunctions.

Finally we observe that the second order method which has been presented in detail in Section II, not only provides an approximate but very convenient way of calculating the energy of a many electron system, but also allows one to discuss many of the correlation effects in simple physical terms as shown above.

VI. Higher Order Correlation Effects

For simplicity the treatment presented in this article has been (so far) confined to second order. In second order, correlations among more than two particles at a time are introduced only by the "exclusion" terms. For three and more body "coulomb" correlations it is necessary to go to higher orders of perturbation.[30] In the system of a single electron outside closed shells, some third order correlation effects influencing the "core-polarization" energy (e.g. in Na) can be introduced into U_f as an additional potential by methods similar to those in Section II, or by letting the mean excitation energy," $\bar{\delta}_C$ absorb the higher order effects semi-empirically. A similar situation occurs in London forces[8,23] where the corresponding mean energies are found to be about twice as large as the ionization potentials of interacting systems with more than two electrons.

An interesting case where higher order correlations deserve further examination is a non-degenerate system of two electrons outside large

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[30] Actually at least for the light atoms the empirical work of Arai and Onishi suggests the pairwise additivity of correlation effects. See:

T. Arai and T. Onishi, J. Chem. Phys. **26**, 70 (1957).

closed shells as in Ca. Here aside from the "exclusion" effects there would be a U_f from the core acting on each of the *4s* electrons, and a "fluctuation potential" $(\overline{r_{12}^{-2}}^{(4s)} - (\overline{r_{12}^{-1}}^{(4s)})^2) / \bar{\Delta}$ (as in Eq. (41)) acting between the two (*4s*) electrons (similar to the correlation of $(1s)^2$ in He). However the presence of a large polarizable core inside introduces additional effective interactions between the two outer electrons in higher orders as can be seen by a crude but suggestive classical argument. Consider the core as a charge sphere with polarizability α and assume the two outer electrons to be momentarily at rest (see Eq. (1)) at distances r_1 and r_2 from the nucleus with an angle θ_{12} between them. Then each electron induces a dipole moment of α/r_1^2 at the core with which it interacts to yield an energy $-\alpha/2r_1^4$ or the limit of U_f in Eq. (46) as r_1 approaches infinity. But in addition, the dipole induced by the electron at r_1 acts on the electron at r_2 giving $[t_{12}^{(3)} \sim -\alpha \cos \theta_{12}/r_1^2 r_2^2]$. It is interesting to note the similarity of this additional interaction between the $(4s)^2$, to the new third order interaction[23] introduced between two molecules by the presence of an adsorbing inert solid surface modifying their usual second order "dispersion" attraction.

There is one case where many electron correlations can be easily introduced and this is when two electron groups *A* and *B* may be considered totally separate as in the usual theory of van der Waals' forces.[6,8] In this case we can use second order Schrödinger perturbation theory with the exact many electron eigenfunctions ψ_A^k, ψ_B^ℓ, of the unperturbed independent systems. Then the unperturbed Hamiltonian $\underline{H}_o = \underline{H}_A + \underline{H}_B$, the basis set $\psi_{k\ell} = \psi_A^{\,k}\,\psi_B^{\,\ell}$ and the perturbation is the total interaction between A and B given by

$$V_{AB} = G_{AB} + U_{AB} \qquad (60)$$

where $U_{AB} \equiv \sum_{i,j} \frac{1}{|\underset{\sim}{r}_i^A - \underset{\sim}{r}_j^B|} = \sum_{i,j} \frac{1}{r_{ij}^{AB}}$

,

and

$$G_{AB} \equiv \sum_{I,J} \frac{Z_I\, Z_J}{|\underset{\sim}{R}_I^A - \underset{\sim}{R}_J^B|}$$

G_{AB} refers to the interaction between the nuclei in A and the nuclei in B. U_{AB} is the electrostatic potential between pairs of electrons one in A (at $\underset{\sim}{r}_i^A$) and the other in B ($\underset{\sim}{r}_j^B$). $\psi_A^{\,k}$ and $\psi_B^{\,\ell}$ are the set of exact eigenfunctions of the isolated systems A and B and include the coordinates of all the electrons and even the nuclei localized at A or B respectively.[23] Then the inter-group "dispersion" energy is given by:

$$E^{(2)}_{disp.}\,(AB) = -\sum_{\substack{k \neq 0\\ \ell \neq 0}} \frac{<\psi_A^{\,o}\,\psi_B^{\,o},\, V_{AV}\,\psi_A^{\,k}\,\psi_B^{\,\ell}>^2}{\delta_A^{\,ok} + \delta_B^{\,o\ell}} \equiv -\sum_{\substack{k \neq 0\\ \ell \neq 0}} \frac{<oo,\, V_{AB}\, k\ell>^2}{\delta_A^{\,ok} + \delta_B^{\,o\ell}}$$

where e.g. $\delta_A^{\,ok} = E_A^{\,k} - E_A^{\,o}$ and $H_A\,\psi_A^{\,k} = E_A^{\,k}\,\psi_A^{\,k}$. Replacing the denominator by "mean excitation energies" and using Eq. (27) we get:

$$E^{(2)}_{\text{disp.}}\ (AB) \approx (\bar{\delta}_A + \bar{\delta}_B)^{-1} \left(< oo,\ V^2_{AB}\ \ oo > - < o,\ W_A^{\ 2}\ o > \right.$$

$$\left. - < o,\ W_B^{\ 2}\ o > + < oo,\ V_{AB}\ oo >^2 \right)$$

where e.g.

$$< o,\ W_A^{\ 2}\ o > = < \ \psi_B^{\ o},\ W_A^{\ 2}\ (\underset{\sim}{R}_B)\ \psi_B^{\ o} >$$

and

$$W_A\ (\underset{\sim}{R}_B) = \int \ |\ \psi_A^{\ o}\ (\underset{\sim}{R}_A)\ \ |^2\ \ U_{AB}\ d\tau_A \qquad (63)$$

with e.g. $\underset{\sim}{R}_A$ denoting all $\underset{\sim}{r}_i^A$ and $\underset{\sim}{R}_I^A$. If A and B are neutral systems, the last three terms of Eq. (62) may be negligible since they depend on the static charge distributions of A and B. Then Eq. (62) takes on the form of the "fluctuation potential" of one system acting on the other; i.e.

$$E^{(2)}_{\text{disp.}}\ (AB) \approx - \frac{< oo,\ V^2_{AB}\ oo >}{\bar{\delta}_A + \bar{\delta}_B} \qquad (64)$$

Thus the "dispersion" energy between two isolated groups is similar to the "core-polarization" energy (neglecting exchange and overlap) when $\delta_B < \delta_A$. Same treatment of course applies to the scattering of electrons by atoms as well.[31]

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[31] A. Temkin, Phys. Rev. 107, 1004 (1957)

Consider now only the U_{AB} part of V_{AB} (Eq. (60)) and in Eq. (64) write U_{AB}^2 in detailed form:

$$U_{AB}^2 = \Big(\sum_{i,j} \frac{1}{r_{ij}^{AB}}\Big)^2 = \sum_{i,j}\Big(\frac{1}{r_{ij}^{AB}}\Big)^2 + \sum_{i,j\neq r,s}\Big(\frac{1}{r_{ij}^{AB}\, r_{rs}^{AB}}\Big) \qquad (65)$$

Here i and r are electrons in *A* and j and s are electrons in *B*. The $(r_{ij}^{AB})^2$ terms in Eq. (65) involve the coordinates of only one electron at a time from each group and their contribution to Eq. (64) can be written in terms of the first order density matrices of *A* and *B*. Two electrons i and r from *A* enter along with one or two electrons (j and s) from *B* into the $(r_{ij}^{AB}\, r_{rs}^{AB})$ terms and their contribution is in terms of the second order density matrices of *A* and *B*.[23,32] Thus since ψ_A^o and ψ_B^o are exact many electron *functions*, the effects of the internal correlations of each group on $E_{disp}^{(2)}$ (AB) has been brought in.

In the same way it may be thought feasible to use many electron functions to discuss the interactions between overlapping groups, such as the shells of the *Be* atom, to introduce higher order correlations. But now, since the groups can't really be separated, it becomes necessary to use "generalized orthogonality conditions."[10,33] These conditions are too

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32. J. Bardeen, Phys. Rev. *58*, 727 (1940).

33. P. G. Lykos and R. G. Parr, J. Chem. Phys. *24*, 1166 (1956).

restrictive since they imply the subdivision a one electron basis set into mutually exclusive subsets, one subset for each group. The degree of such a restriction becomes particularly apparent when e.g. *Be* is considered instead of the σ - π problem. Thus a separation of electron groups based on a complete single electron basis set as in Section II, seems more plausible.

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