

## Electron affinities by a variation-perturbation approach

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A simple variation-perturbation method recently developed is applied to the calculation of electron affinities. In this method a common basis is used for both the ion and the neutral system. The resulting secular equations are of a very small dimension. The matrix elements entering these equations can be evaluated by diagrammatic methods. The formalism is compared with the one-body Green's function method. The electron affinities of Li, Na, F, Cl, and OH are calculated.

### I. INTRODUCTION

Electron affinities (EA's) are of interest both from the experimental and the theoretical point of view. Traditionally it has been difficult to measure these quantities accurately so that theoretical predictions are of great value.<sup>1</sup> Laser detachment spectroscopy brought a breakthrough in accurate experimental determination of EA's of several atoms and a few molecules.<sup>2</sup> There is still a wide range of atomic and molecular systems where an accurate measurement of the EA is not yet possible. Unfortunately it is also difficult to compute accurate EA's via *ab initio* methods. The difficulties which arise are clearly brought out by Sasaki and Yoshimine,<sup>3</sup> who performed large-scale variational calculations on first-row atoms. Such extensive calculations can hardly be performed on larger systems, where accurate EA's are unknown. It is therefore of interest to study different approaches with respect to their ability to predict EA's.

In the traditional approach to calculate the EA of an atom or molecule  $M$  from first principles one computes separately the ground-state energies  $E$  of  $M$  and of the ion  $M^-$  and obtains the EA upon subtraction. There exist also several promising attempts to calculate the EA directly, e.g., the equation-of-motion<sup>4</sup> and the Green's-function<sup>5</sup> methods. The essential advantage of the direct methods is that they avoid the subtraction of large numbers (total energies) of roughly equal magnitude, as is done in the traditional approach. Here we try to incorporate this advantage of the direct approach into the traditional one.

The formalism used here is a combination of variation and perturbation theory and has been found very promising even in the case of large

perturbation.<sup>6</sup> Up to now it has been applied to the anharmonic oscillator,<sup>7</sup> to the hydrogen atom,<sup>6</sup> where the whole Coulomb potential is taken as a perturbation, and to the correlation problem in molecules<sup>8</sup> also for larger internuclear distances. In each order of the perturbation the formalism contains as special cases the Rayleigh-Schrödinger and the Brillouin-Wigner expansions, the Goldhammer-Feenberg<sup>9</sup> refinement of the Brillouin-Wigner series, and the analogous refinement of the Rayleigh-Schrödinger series,<sup>10</sup> as well as the continued-fraction expansion of the resolvent matrix element. The variation-perturbation method to calculate EA's is presented in Sec. II and compared to the Green's-function method in Sec. III. In Sec. IV the numerical results are discussed.

### II. THEORY

For the theoretical development we use the occupation-number formalism, where  $a_k$  is a destruction operator for a fermion in the one-particle state specified by the index  $k$ . The Hamiltonian  $H$  of an atom or molecule can be decomposed as

$$H = H_0 + V. \quad (1)$$

By choosing the unperturbed Hamiltonian  $H_0$  to be the Hartree-Fock (HF) operator,  $H_0$  and  $V$  become

$$H_0 = \sum \mathcal{E}_k a_k^\dagger a_k, \quad (2)$$

$$V = \frac{1}{2} \sum V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k - \sum v_{ij} a_i^\dagger a_j,$$

where the  $\mathcal{E}_k$  denote the one-particle HF energies and the matrix elements  $V_{ijkl}$  and  $v_{ij}$  are given

by

$$V_{ijkl} = \langle i(1)j(2) | r_{12}^{-1} | k(1)l(2) \rangle,$$

$$v_{ij} = \sum_{I=1}^N V_{iI[jI]},$$

$$V_{ij[kl]} = V_{ijkl} - V_{ijlk}.$$

$N$  is the number of electrons in the system. The unperturbed energy  $E_{\text{HF}}^0$  and the HF energy in the HF ground state  $|\text{HF}\rangle$  are

$$E_{\text{HF}}^0 \equiv \langle \text{HF} | H_0 | \text{HF} \rangle = \sum_{m=1}^N \mathcal{E}_m, \quad (3)$$

$$E_{\text{HF}} \equiv \langle \text{HF} | H | \text{HF} \rangle = E_{\text{HF}}^0 - \frac{1}{2} \sum_{m,n=1}^N V_{mn[mn]}.$$

The HF operator is not always the best choice of the unperturbed Hamiltonian, but is the most common choice. The formalism does not depend on this choice.

The simplest expression for the wave function obtained by the variation-perturbation approach<sup>6</sup> reads ( $Q = 1 - |\text{HF}\rangle\langle \text{HF}|$ )

$$|\psi\rangle = |\text{HF}\rangle + \gamma \frac{Q}{\bar{\mathcal{E}} - H_0} V |\text{HF}\rangle, \quad (4)$$

with variational parameters  $\gamma$  and  $\bar{\mathcal{E}}$ . From this we obtain for the ground state energy  $E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$  the simple expression

$$\begin{aligned} \bar{E} &= \frac{1}{2} \left( \frac{E_3 - E_2}{S} + \mathcal{E} \right) - \left[ \frac{1}{4} \left( \frac{E_3 - E_2}{S} + \mathcal{E} \right)^2 + \frac{E_2^2}{S} \right]^{1/2}, \\ \bar{E} &= E - E_{\text{HF}}, \quad \mathcal{E} = \bar{\mathcal{E}} - E_{\text{HF}}^0, \end{aligned} \quad (5)$$

where

$$\begin{aligned} E_2 &= \langle \text{HF} | V \frac{Q}{\bar{\mathcal{E}} - H_0} V | \text{HF} \rangle, \\ S &= \langle \text{HF} | V \frac{Q}{(\bar{\mathcal{E}} - H_0)^2} V | \text{HF} \rangle, \\ E_3 &= \langle \text{HF} | V \frac{Q}{\bar{\mathcal{E}} - H_0} V \frac{Q}{\bar{\mathcal{E}} - H_0} V | \text{HF} \rangle - (E_{\text{HF}} - E_{\text{HF}}^0) S. \end{aligned} \quad (6)$$

To calculate such matrix elements with the Hamiltonian (2) one can use a diagrammatic method described in the Appendix.

In principle the EA,  $E(M) - E(M^-)$ , can be evaluated from two separate calculations of the type described above, one for the molecule  $M$  and one for the ion  $M^-$ . In this way one is faced again with the subtraction of large numbers of roughly equal magnitude. By starting from two different *finite*-basis-set HF calculations, one actually deals with two different Hamiltonians and as a consequence the ground-state energies  $E(M)$  and  $E(M^-)$  are obtained on a different level of accuracy. Thus it should be of advantage to

start from a single HF calculation for both systems and to derive expressions for  $E(M)$  and  $E(M^-)$  which have explicitly in common the large numbers appearing in the calculations, e.g.,  $E_{\text{HF}}^0, E_{\text{HF}}$ , and those parts of the correlation energies which are roughly equal for both systems.

We choose the HF one-particle wave functions of the ion  $M^-$  to be the basis for the Hamiltonian (2). If one starts from the molecule as the reference system, then the energy of an *unoccupied* orbital is the first-order approximation to the EA. By choosing the ion as the reference system an *occupied* orbital is related to the EA. Unoccupied orbitals are usually much more sensitive to the choice of the basis set than are occupied orbitals. In addition the energy of the lowest unoccupied orbital is known to be a poor approximation to the EA. On the other hand, we shall see in Sec. IV that the energy of the highest occupied orbital provides a reasonable first-order approximation to the EA.

Li is a useful example to study the choice of the reference system. The negative value of the energy of the lowest unoccupied orbital of Li calculated in the RHF (restricted HF) scheme is<sup>11</sup> 5.34 eV, whereas the negative value of the energy of the highest occupied orbital of  $\text{Li}^-$  calculated with the same scheme is 0.40 eV. The experimental EA of Li is<sup>12</sup> 0.620 eV. It seems that more information about the EA of  $M$  is included in the HF calculation of  $M^-$  than in the corresponding calculation of  $M$ .

It is also interesting to note that the EA of Li obtained by performing two separate HF calculations, one for Li and one for  $\text{Li}^-$ , is<sup>11</sup> -0.122 eV. This underlines the importance of having a common starting point for both systems and of calculating the total energies on about the same level of accuracy.

A further though only formal reason for choosing the ion as the reference system is that several systems with EA's of interest have negative ions with a nondegenerate ground state. For such systems the RHF scheme is the appropriate one to use, i.e., there is no symmetry dilemma,<sup>13</sup> and since  $\langle r_1, \dots, r_N | \text{HF} \rangle$  is one Slater determinant, all expressions simplify. For simplicity we restrict ourselves in the following to ions with a nondegenerate ground state. The generalization to degenerate ground states is straightforward.

Let us now return to Eq. (4) and rewrite the expression for the ground state of the ion  $M^-$ . With the Hamiltonian (2) one easily finds

$$|\psi\rangle = |\text{HF}\rangle + \frac{1}{4}\gamma \sum_{\substack{i,j \leq N \\ m,n > N}} \frac{V_{mn[ji]}}{\mathcal{E}_{mnji}} a_m^\dagger a_n^\dagger a_i a_j |\text{HF}\rangle, \quad (7)$$

where

$$\mathcal{E}_{mnji} = \mathcal{E} - \mathcal{E}_m - \mathcal{E}_n + \mathcal{E}_j + \mathcal{E}_i.$$

By eliminating one electron in the HF ground state of the ion  $M^-$  a suitable reference state  $|k\rangle$  for the molecule  $M$  is obtained,

$$|k\rangle = a_k | \text{HF} \rangle. \quad (8)$$

In the lowest possible approximation the EA takes the form

$$\begin{aligned} \text{EA} &= \langle k | H_0 | k \rangle - \langle \text{HF} | H_0 | \text{HF} \rangle \\ &= E_{\text{HF}}^0 - \mathcal{E}_k - E_{\text{HF}}^0 = -\mathcal{E}_k, \end{aligned} \quad (9a)$$

which is the same result as obtained in the first-order approximation

$$\begin{aligned} \text{EA} &= \langle k | H | k \rangle - \langle \text{HF} | H | \text{HF} \rangle \\ &= E_{\text{HF}} - \mathcal{E}_k - E_{\text{HF}} = -\mathcal{E}_k. \end{aligned} \quad (9b)$$

This result has been found to provide a reasonable approximation to the EA if  $k$  is the highest oc-

$$| \phi \rangle = \sum_k \left[ \gamma_{0k} a_k | \text{HF} \rangle + \gamma_{1k} \left( \frac{1}{2} \sum_{\substack{m,i \leq N \\ i > N}} \frac{V_{ik[im]}}{\mathcal{E}_{ikhlm}} a_i^\dagger a_m a_i | \text{HF} \rangle + \frac{1}{4} \sum_{\substack{m,i \leq N \\ i,j > N}} \frac{V_{ij[im]}}{\mathcal{E}_{ijlm}} a_i^\dagger a_j^\dagger a_m a_i a_k | \text{HF} \rangle \right) \right]. \quad (11)$$

We have seen that  $|\psi\rangle$  in Eq. (7) contains doubly excited configurations with respect to the unperturbed ground state. The state  $|\phi\rangle$  also contains doubly excited configurations with respect to all  $|k\rangle$ , but in addition contains singly excited configurations with respect to  $|1\rangle$ , where the index 1 runs over all orbitals occupied in the ground state of  $M^-$ .

By denoting  $|k\rangle$  by  $|0\rangle_k$ , the term of the wave function having three fermion operators by  $|1\rangle_k$ , and the last term in (11) by  $|2\rangle_k$ , we may write

$$| \phi \rangle = \sum_k (\gamma_{0k} | 0 \rangle_k + \gamma_{1k} | 1 \rangle_k + \gamma_{2k} | 2 \rangle_k), \quad (12)$$

where an additional variational parameter  $\gamma_{2k}$  has been introduced to allow for the separate variation of the singly and doubly excited configurations. With Eq. (12) we have to solve a secular equation which is  $\frac{3}{2}$  times larger than the secular equation obtained from Eq. (11), but no new matrix elements have to be evaluated.

If  $K$  is the number of states  $|k\rangle$  taken into account, Eq. (12) leads to the following secular equation for the energy of  $M$ :

$$(\underline{H} - E \underline{S}) \underline{\gamma} = 0, \quad (13)$$

where  $\underline{H}$  and  $\underline{S}$  are  $3 \times 3$  matrices with submatrices  $H_{ij}$  and  $S_{ij}$  of dimension  $K$ . The submatrices  $S_{ij}$  and  $H_{ij}$  have elements  $(S_{ij})_{kk'}$  and  $(H_{ij})_{kk'}$  which are simply given by  ${}_k \langle i | j \rangle_{k'}$  and

cupied orbital.

In complete analogy to Eq. (4) the ground state  $|\phi\rangle$  of  $M$  can be written as  $(Q = 1 - |k\rangle \langle k|)$ ,

$$| \phi \rangle = | k \rangle + \gamma \frac{Q}{\mathcal{E} - H_0} V | k \rangle. \quad (10a)$$

This result can easily be generalized to the case where several states  $|k\rangle$  of the same symmetry interact with each other ( $Q = 1 - \sum |k\rangle \langle k|$ ),

$$| \phi \rangle = \sum_k \left( \gamma_{0k} | k \rangle + \gamma_{1k} \frac{Q}{\mathcal{E} + E_{\text{HF}}^0 - \mathcal{E}_k - H_0} V | k \rangle \right). \quad (10b)$$

All the numerical calculations discussed in Sec. IV have been performed with Eq. (10a), which is a special case of (10b). Nevertheless we would like to continue the theoretical investigation with Eq. (10b), which might prove important for larger systems.

Using Eq. (2) we arrive at

${}_k \langle i | H | j \rangle_{k'}$ ,  $i, j = 0, 1, 2$ , respectively. In most actual cases  $K$  is 1 or 2 and  $H$  and  $S$  are  $3 \times 3$  or  $6 \times 6$  matrices only. In the Appendix it is shown how explicit expressions for  $\underline{H}$  and  $\underline{S}$  can be obtained.

It can be shown that  $\underline{H}$  can be decomposed according to

$$\underline{H} = \underline{\tilde{H}} + E_{\text{HF}} \underline{S}, \quad (14)$$

where  $\underline{\tilde{H}}$  does not include  $E_{\text{HF}}$  any more, e.g.,  $(H_{11})_{kk'} = (E_{\text{HF}} - \mathcal{E}_k) \delta_{kk'}$ , and  $(S_{11})_{kk'} = \delta_{kk'}$ . We may now obtain  $\underline{\tilde{E}} = \underline{E} - E_{\text{HF}}$  by solving the secular equation for  $\underline{\tilde{H}}$ ,

$$(\underline{\tilde{H}} - \underline{\tilde{E}} \underline{S}) \underline{\gamma} = 0. \quad (15)$$

The EA is now given by

$$\text{EA} = E(M) - E(M^-) = \underline{\tilde{E}}(M) - \underline{\tilde{E}}(M^-), \quad (16)$$

where  $\underline{\tilde{E}}(M)$  is obtained with Eq. (15) and  $\underline{\tilde{E}}(M^-)$  with the aid of Eq. (5). The final result is thus independent of the total HF energy  $E_{\text{HF}}$ .

We have attempted above to obtain compact expressions for the ground-state energies of  $M$  and  $M^-$  which lead to reasonably accurate EA's. Only the simplest form of the perturbation-variation formalism<sup>6</sup> has been used. There are many ways to improve the individual energies together with the EA itself. One possibility is to start from several reference states instead of starting from  $|\text{HF}\rangle$  alone. The numerical effort in such a pro-

cedure is negligible compared to the effort introduced when the next-order wave function is used.

### III. COMPARISON WITH THE GREEN'S-FUNCTION METHOD

Since the Green's-function method has considerable success in predicting ionization potentials of atoms and molecules, it is of interest to compare it with the present method. The one-particle Green's-function matrix  $\underline{G}(\omega)$  has poles at  $\omega$  values which are equal, up to the sign, to the ionization potentials and EA's of the system under consideration. To find the poles of  $\underline{G}(\omega)$  it is convenient to start from the well-known Dyson equation<sup>14</sup>

$$\underline{G} = \underline{G}^0 + \underline{G}^0 \underline{M} \underline{G}, \quad (17)$$

which relates the Green's function to the self-energy part  $\underline{M}(\omega)$ .  $\underline{G}^0$  is the free Green's function with elements

$$G_{ij}^0(\omega) = \delta_{ij}/(\omega - \mathcal{E}_i). \quad (18)$$

Considering only a diagonal self-energy part, one obtains for the EA (the ion  $M^-$  is the reference system)

$$\begin{aligned} EA &= -\mathcal{E}_k - M_{kk}(-EA) \\ &= -\mathcal{E}_k - M_{kk}(\mathcal{E}_k) + O(V^4). \end{aligned} \quad (19)$$

The terms of the expansion of  $\underline{M}(\omega)$  up to third order in the interaction  $V$  are discussed in detail in the literature.<sup>15</sup>

To compare with the variation-perturbation method we put, for the sake of simplicity,  $\gamma_{2k} = \gamma_{1k}$  as suggested by Eq. (11). As was done for the self-energy part in Eq. (19) we choose  $|\phi\rangle$  to include only one reference state  $|k\rangle$ . Then  $\underline{\tilde{H}}$  and  $\underline{\tilde{S}}$  in Eq. (15) become  $2 \times 2$  matrices. If the perturbation expansion converges rapidly, we may put the variational parameter  $\mathcal{E}$  equal to zero, which is the value proposed by the Rayleigh-Schrödinger expansion, and obtain

$$\begin{aligned} \tilde{H}_{00} &= -\mathcal{E}_k, \\ \tilde{H}_{01} = \tilde{H}_{10} &= -M_{kk}^{(2)}(\mathcal{E}_k) + E_2, \\ \tilde{H}_{11} &= -\tilde{H}_{01} - M_{kk}^{(3)}(\mathcal{E}_k) + E_3 - \mathcal{E}_k S_{11}, \end{aligned} \quad (20)$$

where  $\underline{M}^{(2)}$  and  $\underline{M}^{(3)}$  are the second- and third-order terms in the expansion of  $\underline{M}$ , and  $E_2$  and  $E_3$  are given in Eq. (6).

From Eq. (5) it follows for  $\mathcal{E} = 0$ ,

$$\tilde{E}(M^-) = E_2 + E_3 + O(V^4), \quad (21a)$$

and from Eqs. (15) and (20) we get at  $\mathcal{E} = 0$ ,

$$\begin{aligned} \tilde{E}(M) &= -\mathcal{E}_k - M_{kk}^{(2)}(\mathcal{E}_k) - M_{kk}^{(3)}(\mathcal{E}_k) \\ &\quad + E_2 + E_3 + O(V^4). \end{aligned} \quad (21b)$$

The EA is simply given by

$$EA = -\mathcal{E}_k - M_{kk}^{(2)}(\mathcal{E}_k) - M_{kk}^{(3)}(\mathcal{E}_k) + O(V^4), \quad (22)$$

which is identical up to third order with the EA obtained via the Dyson equation (19).

For atoms and molecules it has been found<sup>15</sup> that even if the third-order contribution is large, accurate ionization potentials are obtained by applying a renormalization procedure in which only terms up to third order are needed as input data. This implies that the higher-order contributions are mainly due to terms which "arise" from the second- and third-order terms. Therefore one may gain understanding of how higher orders are included in the present formalism by comparing the  $\tilde{H}_{ij}$ ,  $i, j = 0, 1, 2$ , with the individual contributions of the Feynman diagrams of  $\underline{M}$  in its expansion up to third order.

To be able to proceed some information is needed about the individual time-ordered Feynman diagrams<sup>14,16-18</sup> appearing in the expansion of  $\underline{M}$  up to third order. We follow here the nomenclature introduced in Ref. 15, where these diagrams are discussed in detail. In second order there are two time-ordered Abrikosov diagrams<sup>16</sup> (an Abrikosov diagram contains several Feynman diagrams). Their contributions are given by<sup>14</sup>

$$\begin{aligned} M_{kk}^{(2)}(1) &= \frac{1}{2} \sum_{\substack{n,l \leq N \\ m > N}} \frac{V_{km[nl]} V_{k'm[nl]}}{\omega + \mathcal{E}_m - \mathcal{E}_n - \mathcal{E}_l}, \\ M_{kk}^{(2)}(2) &= \frac{1}{2} \sum_{\substack{n,l > N \\ m \leq N}} \frac{V_{km[nl]} V_{k'm[nl]}}{\omega + \mathcal{E}_m - \mathcal{E}_n - \mathcal{E}_l}. \end{aligned} \quad (23)$$

In third order there are three Abrikosov diagrams, one of them, denoted by  $A$ , is independent of  $\omega$ . The remaining diagrams are a ladder-type diagram, denoted by  $C$ , and an RPA- (random-phase-approximation-) type diagram denoted by  $D$ . Each of these diagrams has six time-ordered diagrams  $A_1-A_6, C_1-C_6, D_1-D_6$ .

For  $\mathcal{E} = 0$  the elements of  $\tilde{H}_{ij}$ ,  $i, j = 0, 1, 2$ , in Eq. (15) can now be explicitly written as

$$\begin{aligned} \tilde{H}_{00} &= -\mathcal{E}_k, \\ \tilde{H}_{01} = \tilde{H}_{10} &= -M_{kk}^{(2)}(1), \\ \tilde{H}_{02} = \tilde{H}_{20} &= -M_{kk}^{(2)}(2) + E_2, \\ \tilde{H}_{12} = \tilde{H}_{21} &= -(A_3 + A_5 + C_4 + D_4), \\ \tilde{H}_{11} &= -(C_6 + D_6) + M_{kk}^{(2)}(1) - \mathcal{E}_k S_{11}, \\ \tilde{H}_{22} &= -[C_1 + D_1 + 2(C_2 + D_2) + A_1 + A_2] \\ &\quad + M_{kk}^{(2)}(2) - E_2 + E_3 - \mathcal{E}_k S_{22}. \end{aligned} \quad (24)$$

It should be noted that for  $k=k'$ , which is assumed here, the following relations hold:  $A_3=A_4, A_5=A_6, C_2=C_3, D_2=D_3, C_4=C_5, D_4=D_5$ . All the contributions of the diagrams in Eq. (24) are for  $\omega = \mathcal{E}_k$ .

It has been shown<sup>15</sup> that among the time-ordered diagrams of third order there are pairs of diagrams which nearly compensate each other, e.g.,  $C_6$  and  $D_6$ . The only diagrams which (for  $k \leq N$ ) are *not* members of these pairs are  $A_3, A_5, C_4$ , and  $D_4$ . These diagrams, especially  $D_4$ , play an important role in the renormalization procedure. It is therefore instructive to see that also in the present approach all these diagrams are collected in one element, namely,  $\tilde{H}_{12}$ .

As soon as the value of  $\mathcal{E}$  obtained via variation of the energy is far from zero, a simple comparison of both methods cannot be made. It is noteworthy that the quantity  $\mathcal{E}$  enters the expres-

sions given in Eq. (24) in a completely different way than does the quantity  $\omega$  in the self-energy part. A demonstrative example is supplied by a comparison with the self-energy part of second order as given in Eq. (23). The term  $-\tilde{H}_{10}$  in Eq. (24) becomes

$$\frac{1}{2} \sum_{\substack{n,i \leq N \\ m > N}} \frac{V_{km[ni]} V_{km[ni]}}{-\mathcal{E} + \mathcal{E}_k + \mathcal{E}_m - \mathcal{E}_n - \mathcal{E}_i},$$

i.e.,  $\omega \rightarrow \mathcal{E}_k - \mathcal{E}$ , while the term  $E_2 - \tilde{H}_{20}$  becomes

$$\frac{1}{2} \sum_{\substack{n,i > N \\ m \leq N}} \frac{V_{km[ni]} V_{km[ni]}}{+\mathcal{E} + \mathcal{E}_k + \mathcal{E}_m - \mathcal{E}_n - \mathcal{E}_i},$$

i.e.,  $\omega \rightarrow \mathcal{E}_k + \mathcal{E}$ . In addition one finds those terms in  $\tilde{H}$  which are equal to  $A_1 - A_6$  for  $\mathcal{E} = 0$  to depend on  $\mathcal{E}$ , while the corresponding Feynman diagrams in the expansion of  $\underline{M}$  do not depend on  $\omega$ , e.g.,

$$A_1 \rightarrow -\frac{1}{2} \sum_{\substack{t,r,s \leq N \\ a,b > N}} \frac{V_{kr[kt]} V_{ts[ab]} V_{ab[rs]}}{(\mathcal{E} + \mathcal{E}_s + \mathcal{E}_t - \mathcal{E}_a - \mathcal{E}_b)(\mathcal{E} + \mathcal{E}_s + \mathcal{E}_r - \mathcal{E}_a - \mathcal{E}_b)}. \quad (25)$$

#### IV. RESULTS AND DISCUSSION

The variation-perturbation method described above has been applied to calculate the EA's of the atoms Li, Na, F, and Cl, and of the molecule OH. The calculation of the self-consistent-field (SCF) wave function has been performed with the program system MUNICH,<sup>19</sup> expanding the orbitals in Cartesian Gaussian functions. In the variation-perturbation part of the computation the linear variational parameters  $\gamma$  were determined by matrix diagonalization, while the optimum value of the nonlinear parameter  $\mathcal{E}$  was obtained by a pointwise calculation of the  $\tilde{E}(\mathcal{E})$  curves with a small set of virtual orbitals. The set of virtual orbitals was subsequently enlarged and  $\mathcal{E}$  re-determined. When  $\mathcal{E}$  was found to be constant this value was used in the final calculation exhausting the basis set.

The influence of different basis sets on the quality of the computed EA's was studied for the F atom. For the  $s$ - $p$  part of the basis set the  $(11s/7p)/[5s/4p]$  basis of Salez and Veillard<sup>20</sup> was considered to be flexible enough except for the long-range part of the wave function. Thus an additional  $s$ -type function with exponential parameter  $\alpha_s(\text{F}) = 0.05$  and an additional  $p$ -type function [ $\alpha_p(\text{F}) = 0.05$ ] were added. Care was taken in this as well as in all other calculations that the  $s$ - and  $p$ -type functions with the smallest exponential parameters were only used to a small extent in the expansion of the occupied molecular orbitals (MO's) so that a correct long-range be-

havior could be obtained. The basis set for the F atom thus consists of six  $s$ -type and five  $p$ -type contracted functions. The total SCF energy obtained with this basis set is  $E_{\text{tot}}^{\text{SCF}} = -99.448855$  a.u. and the orbital energy of the  $2p$  orbital is  $-4.93$  eV. To this basis  $d$ - and  $f$ -type functions were added. The different sets used are listed in Table I. From two to four  $d$ -type functions were employed and different sets of exponential parameters were tried. Since the  $\text{F}^-$  ion has a diffuse charge distribution in contrast to the neutral F atom it is expected that correlation energy changes arise from this difference. Consequently, relatively diffuse  $d$ -type functions have been included in the basis.  $f$ -type functions have been added to a basis with two and another one with three  $d$ -type functions. Table II contains the results of the calculations with the different basis sets. From basis I to basis VI the correlation

TABLE I. Basis sets used in the calculation of the EA of F. For the exponential parameters of the  $s$ - $p$  basis set see text.

Basis	Uncontracted basis set	Contracted basis set	$\alpha_d$	$\alpha_f$
I	12s8p2d	6s5p2d	1.23, 0.3	...
II	12s8p2d1f	6s5p2d1f	1.23, 0.3	0.5
III	12s8p3d	6s5p3d	1.8, 0.6, 0.2	...
IV	12s8p4d	6s5p4d	2.2, 1.0, 0.4, 0.15	...
V	12s8p4d	6s5p4d	5.4, 1.8, 0.6, 0.2	...
VI	12s8p3d1f	6s5p3d1f	1.8, 0.6, 0.2	1.0

TABLE II. Variation of the electron affinity of F with basis set ( $\mathcal{E}$  given in a.u., all other quantities in eV.)

Basis	$E_c^a$	$\mathcal{E}(F^-)$	EA	$\mathcal{E}(F)$	$E(F) - \hat{E}(F^-)^b$
I	-5.739	-0.8	3.67	-2.5	3.58
II	-5.988	-0.7	3.73	-2.5	3.67
III	-6.389	-0.8	3.68	-3.0	3.58
IV	-6.491	-0.8	3.68	-3.0	3.57
V	-6.706	-0.8	3.65	-3.0	3.52
VI	-7.065	-0.8	3.74	-3.0	3.62

<sup>a</sup>  $E_c$  is the valence correlation energy of  $F^-$  calculated with Eq. (5).

<sup>b</sup>  $\hat{E}(F^-)$  is  $E(F^-)$  calculated at  $\mathcal{E} = \mathcal{E}(F)$  (see text).

energy of the  $F^-$  ion changes by about 1.3 eV, but the EA changes by a much smaller amount, only by about 0.1 eV. When considering only the calculations with different  $d$ -type functions the variation in the EA is only 0.03 eV. The EA is thus found to be stable with respect to the variation of both the number and the exponential parameters of the  $d$ -type functions. The error with respect to the experimental value of<sup>21</sup> 3.448 eV is 0.2 to 0.23 eV. When  $f$ -type functions are added the EA increases and the error is about 0.3 eV.  $f$ -type functions (at least as chosen here) are thus more important for the description of the correlation energy in the  $F^-$  ion than in the neutral atom.

Using a large basis set of Slater-type functions up to  $i$ -type, Sasaki and Yoshimine<sup>3</sup> computed a valence correlation energy of 8.19 eV for  $F^-$  by a configuration-interaction calculation including all single and double substitutions, and 8.47 eV including triple and quadruple substitutions as well, which they estimate to be about 95% of the total valence correlation energy. The present result for the correlation energy (7.07 eV) is thus 85% of the corresponding value of Sasaki and Yoshimine.

The optimum value of  $\mathcal{E}$  is  $-0.7$  to  $-0.8$  a.u. for the ion and  $-2.5$  to  $-3.0$  a.u. for the F atom. The two values are thus very different. The variation of  $\mathcal{E}$  turns out to be considerably more important for the neutral atom than for the ion, for which the correlation energy is a very flat function of  $\mathcal{E}$  around the optimum value. The neutral atom is in the present method described with the orbital basis of  $F^-$  and the parameter  $\mathcal{E}$  in part corrects for this. Choosing  $\mathcal{E}(M^-)$  to be the same as  $\mathcal{E}(M)$  leads, because of the flat character of the curve, only to slight changes in the EA's. This procedure results in computational savings and tends to improve the computed EA's. The corresponding results for the F atom are given in the column headed  $E(F) - \hat{E}(F^-)$  in Table II. The

EA's are smaller by about 0.1 eV and thus agree better with experiment. The reason for this is that there is in the present method a tendency to describe the  $M^-$  ion better than the neutral  $M$ ; the EA's thus tend to be too large. Using now the  $\mathcal{E}(M)$  value for the ion systematically leads to a poorer description of  $M^-$  and thus to a "better" EA.

Based on the investigation of the EA of the F atom it was decided to use three  $d$ -type functions on all the atoms except for the H atom, where two  $p$ -type functions were employed. It should however, be kept in mind for the calculation of EA's of larger molecules that fewer polarization functions could be used without necessarily deteriorating the quality of the computed EA's. The following basis sets were used in the calculations: Li,  $(13s6p3d)/[8s6p3d]$ ; this is the basis set of Salez and Veillard<sup>20</sup> with two additional  $s$ -type functions ( $\alpha_s = 0.006, 0.002$ ) six  $p$ -type functions ( $\alpha_p = 5.0, 1.2, 0.4, 0.1, 0.25, 0.005$ ), and three  $d$ -type functions ( $\alpha_d = 0.45, 0.15, 0.05$ ). Na,  $(15s10p3d)/[9s6p3d]$ ; this is the basis set of Veillard<sup>22</sup> with three additional  $s$ -type functions ( $\alpha_s = 0.01, 0.004, 0.001$ ), four additional  $p$ -type functions ( $\alpha_p = 0.15, 0.05, 0.015, 0.005$ ), and three  $d$ -type functions ( $\alpha_d = 0.45, 0.15, 0.05$ ). Cl,  $(13s10p3d)/[7s6p3d]$ ; this is the basis set of Veillard<sup>22</sup> with one additional  $s$ -type function ( $\alpha_s = 0.06$ ), one additional  $p$ -type function ( $\alpha_p = 0.035$ ), and three  $d$ -type functions ( $\alpha_d = 1.8, 0.6, 0.2$ ). O,  $(12s8p3d)/[6s5p3d]$ ; this is the basis set of Salez and Veillard with one additional  $s$ -type function ( $\alpha_s = 0.04$ ), one additional  $p$ -type function ( $\alpha_p = 0.025$ ), and three  $d$ -type functions ( $\alpha_d = 1.35, 0.45, 0.15$ ). H,  $(7s/2p)/[4s2p]$ ; this is the basis set of Salez and Veillard with an additional  $s$ -type function ( $\alpha_s = 0.025$ ) and two  $p$ -type functions ( $\alpha_p = 1.2, 0.45$ ). The equilibrium distance of the OH molecule<sup>23</sup> ( $R = 1.834$  a.u.) was employed in order to obtain the vertical EA and not the electron detachment energy. The polarization functions were chosen appropriately to calculate the valence correlation energy in all cases. In the case of Li the  $K$  shell was included in the calculation because it might be inappropriate to treat it as an unpolarizable core. The basis set, on the other hand, was chosen to have maximum flexibility for the  $2s$  orbital. A small part of the  $K$  shell and of the intershell correlation energy will thus only be obtained, but the computation of the total correlation energy of the core does not significantly influence the EA.<sup>3</sup> The inclusion of the  $K$  shell in the calculation supplies the dominant correction to the approximation of an unpolarizable core. The same comment applies to the Na atom, for which the  $L$  shell was included in the calculation.

The results for the total SCF energies, correlation energies (for  $M^-$ ),  $\mathcal{E}$  values, and EA's are presented in Table III. (Note that for the F atom the calculation involving three  $d$ -type functions has been entered for consistency with the other systems.) It is seen that the valence correlation energy for first-row atoms (as F) is considerably larger than for second-row atoms (such as Cl). The  $\mathcal{E}$  values for  $M^-$  and for  $M$  are quite different for the systems and even differ considerably in cases where a greater similarity could be expected (F versus Cl). The calculated EA's are in quite good agreement with the experimental values listed in Table III as well. The errors for Li, Na, and Cl are about 0.04 eV and for F and OH about 0.2 eV. The excellent agreement for the Cl atom is regarded as fortuitous.

Sasaki and Yoshimine<sup>3</sup> found that (a) even with very extended basis sets, which gave about 94 to 95% of the correlation energy for the first-row atoms, only about 83% of the correlation contribution to the EA is obtained and (b) that triple and quadrupole substitutions play a non-negligibly larger role for the ions than for the neutral atoms. The findings of Sasaki and Yoshimine may not entirely apply here. They described the neutral atoms better than the ions resulting in EA's that were too small. In the present scheme the ions are usually better described than the neutrals, which is just the reverse situation resulting in EA's that are too large. Higher than double substitutions might thus give additional flexibility to the neutral system and in the end contribute as much to  $M$  as to  $M^-$  in the present scheme.

There is considerable literature on the calculation of EA's. The theoretical work on EA's of first-row atoms (B to F) has been discussed by Sasaki and Yoshimine<sup>3</sup> in comparing their CI results to other methods. There is further a recent

review article by Hotop and Lineberger<sup>2</sup> on the EA's of atoms with a discussion of various theoretical methods and extensive literature data. The discussion will thus be restricted to work on atoms not mentioned in these two articles and to the EA of the OH molecule. Sims *et al.*<sup>24</sup> performed a very accurate CI calculation on the EA of Li. Estimating relativistic corrections they arrived at an EA of Li of  $0.609 \pm 0.007$  eV, which is so far the most accurate calculation of this quantity and is in very good agreement with the experimental value of  $0.620 \pm 0.007$  eV.<sup>12</sup> Cederbaum and von Niessen<sup>5</sup> computed the EA of Li by a Green's-function method by expanding the self-energy part up to third order. They obtained a value of 0.55 eV with a basis set which is somewhat poorer than the one used in this work.

Staemmler and Jungen<sup>25</sup> used an independent electron-pair approximation to calculate the EA's of first-row atoms. The quality of their results is about the same as in the present variational method. The EA of OH has been determined by Meyer<sup>26</sup> using the variational pseudonatural orbital CI method and extended basis sets, which give a value of 1.265 eV, and the nonvariational coupled-electron-pair approximation, which gives a value of 1.46 eV. Since the latter approximation incorporates the correlation energy contributions of  $2n$ -fold substitutions this tendency is in agreement with the findings of Sasaki and Yoshimine. Smith, Chen, and Simons<sup>27</sup> used the equations-of-motion method for computing the EA of OH. This method is closely related to the Green's-function method. They obtained the very good result of 1.76 eV. They used, however, the wrong distance (minimum of the Hartree-Fock energy curve of OH instead of the distance determined from experiment or CI calculations) and a much-less-extended basis than is used in the present work. Deleting from the basis set of Cade and

TABLE III. Comparison of calculated and observed electron affinities (Total SCF energies and  $\mathcal{E}$  in a.u., all other energies in eV).

System	Orbital						Observed
$M$	energy	$E_{\text{tot}}^{\text{SCF}}(M^-)$	$E_c(M^-)$	$\mathcal{E}(M^-)$	EA	$\mathcal{E}(M)$	EA
Li	0.396	-7.427 97	-1.548 <sup>a</sup>	0.08	0.577	-0.22	0.620 <sup>b</sup>
Na	0.362	-161.821 68	-2.846 <sup>c</sup>	0.08	0.578	-0.12	0.548 <sup>b</sup>
F	4.93	-99.449 61	-6.389 <sup>d</sup>	-0.8	3.68	-3.0	3.448 <sup>e</sup>
Cl	4.09	-459.551 28	-4.806 <sup>d</sup>	-0.2	3.66	-1.2	3.613 <sup>e</sup>
OH	2.98	-75.408 56	-5.674 <sup>d</sup>	-0.7	2.07	-1.5	1.825 <sup>f</sup>

<sup>a</sup> Only a small part of the  $K$ -shell correlation is included (see text).

<sup>b</sup> Reference 12.

<sup>c</sup> Only a small part of the  $L$ -shell correlation is included (see text).

<sup>d</sup> Valence correlation energy.

<sup>e</sup> Reference 21.

<sup>f</sup> Reference 29.

Huo<sup>28</sup> some of the functions which are used to describe the inner shells is justified, but they deleted as well a part of the polarization functions. It would be interesting to repeat their calculations with a larger basis set.

### V. CONCLUSIONS

A variation-perturbation method recently developed is applied in its simplest form to the calculation of EA's. It is argued that a good starting point is obtained by choosing the ion as the reference system and using its orbital basis to construct the Hamiltonian. The wave functions for  $M$  and  $M^-$  consist of the first-order perturbed wave function with linear and a nonlinear variational parameters. The reference state for  $M^-$  is the HF ground state, whereas the reference state for  $M$  is a linear combination of a set of states obtained by annihilating suitable HF particles from the HF ground state. With these wave functions EA's are computed which agree up to the third order in the perturbation with the Green's-function results.

This method has been applied to calculate the EA's of the atoms Li, Na, F, and Cl and of the molecule OH. For Li, Na, and Cl the errors in the computed EA's are about 0.04 eV and for the other systems about 0.2–0.3 eV. The excellent value for Cl is regarded as fortuitous.

The ions are in the present method usually better described than the neutral atoms, yielding somewhat too large EA's, in contrast to the results of Sasaki and Yoshimine, who described the neutral systems better than the ions and thus obtained somewhat too small EA's. In view of the task of determining EA's for larger molecules it appears to the authors to be extremely difficult to calculate accurate EA's via the criterion of best total correlation energies. Sasaki and Yoshimine obtained 94 to 95% of the total correlation energies but only about 83% of the correlation energy change occurring in going from  $M$  to  $M^-$ . It is necessary to aim directly at the correlation energy difference upon electron attachment and describe only this part accurately. In this respect there still remains something to be done. The basis sets used in the present investigation are quite extended, at least what concerns molecular applications. But based on the findings for F it is expected that reasonably accurate EA's could be calculated with less-extended basis sets, which is essential for wider molecular applications.

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### APPENDIX

The matrix elements of  $H$  and the overlap of the wave functions appearing in Secs. II and III can, in principle, be evaluated by simple algebra. This "brute-force" method is, however, very tedious. The situation is very similar to the case of evaluating the Green's function. Here one could, in principle, use the well-known<sup>14,16,17</sup> expansion of  $e^{-iHt}$  to obtain the terms in the expansion of the Green's function. The amount of work which has to be invested is reduced considerably by using the diagrammatic expansion of the Green's function. A similar diagrammatic method is used here to evaluate matrix elements appearing in the variation-perturbation approach.

In the following we denote the HF ground state by  $|1\rangle$  and the doubly excited part of  $|\psi\rangle$  in Eq. (7) by  $|2\rangle$ . The nonvanishing matrix elements of  $H_0$  can be easily calculated directly by using the relations  $a_i^\dagger a_i a_j = a_j a_i^\dagger a_i - a_i \delta_{ij}$  and  $a_i^\dagger a_i a_i^\dagger = a_i^\dagger a_i^\dagger a_i + \delta_{ij} a_i^\dagger$ :

$$\begin{aligned} \langle 1|H_0|1\rangle &= E_{\text{HF}}^0, \\ \langle 2|H_0|2\rangle &= (\mathcal{E} + E_{\text{HF}}^0) \langle 2|2\rangle - \langle 2|V|1\rangle, \\ {}_k \langle 0|H_0|0\rangle_k &= -\mathcal{E}_k + E_{\text{HF}}^0, \\ {}_k \langle 1|H_0|1\rangle_{k'} &= [\mathcal{E} + E_{\text{HF}}^0 - \frac{1}{2}(\mathcal{E}_k + \mathcal{E}_{k'})](S_{11})_{kk'} \\ &\quad - \frac{1}{2}({}_k \langle 1|V|0\rangle_{k'} + {}_k \langle 0|V|1\rangle_{k'}), \\ {}_k \langle 2|H_0|2\rangle_{k'} &= [\mathcal{E} + E_{\text{HF}}^0 - \frac{1}{2}(\mathcal{E}_k + \mathcal{E}_{k'})](S_{22})_{kk'} \\ &\quad - \frac{1}{2}({}_k \langle 2|V|0\rangle_{k'} + {}_k \langle 0|V|2\rangle_{k'}). \end{aligned} \quad (\text{A1})$$

We now decompose  $V$  into its one-particle and two-particle parts:

$$\begin{aligned} V_1 &= -\sum v_{ij} a_i^\dagger a_j, \\ V_2 &= \frac{1}{2} \sum V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \\ &= \frac{1}{4} \sum V_{ij[kl]} a_i^\dagger a_j^\dagger a_l a_k. \end{aligned} \quad (\text{A2})$$

To evaluate the matrix elements diagrammatically symbols must be introduced for  $V_1$ ,  $V_2$  and for the wave functions. These symbols are shown in Fig. 1. The rules to obtain the diagrams which contribute to a given matrix element are given in the following:

(i) Draw the "skeleton" representing the matrix element. A skeleton  $A:B:C$  is obtained by drawing the quantities  $C$ ,  $B$ , and  $A$  below each other.

(ii) Draw all topologically nonequivalent dia-



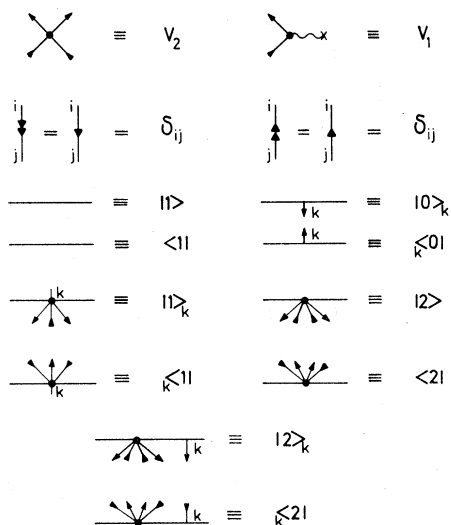


FIG. 1. Definition of symbols used to evaluate matrix elements.  $V_1$  and  $V_2$  are the one-particle and two-particle parts of the interaction  $V$ , respectively.  $|1\rangle$  stands for  $|HF\rangle$  and  $|2\rangle$  for the doubly excited part of  $|\psi\rangle$  in Eq. (7).  $|0\rangle_k$ ,  $|1\rangle_k$ , and  $|2\rangle_k$  are defined by Eq. (12).

grams which can be obtained by connecting the arrows of the skeleton. (If two arrows are connected, a so-called free line results; see Fig. 1.)

A simple example is shown in Fig. 2(a). To obtain the overlap  $\langle 2|2\rangle$  the skeleton  $\langle 2|:|2\rangle$  is drawn on the left-hand side of the figure. There are four possibilities to connect the arrows of

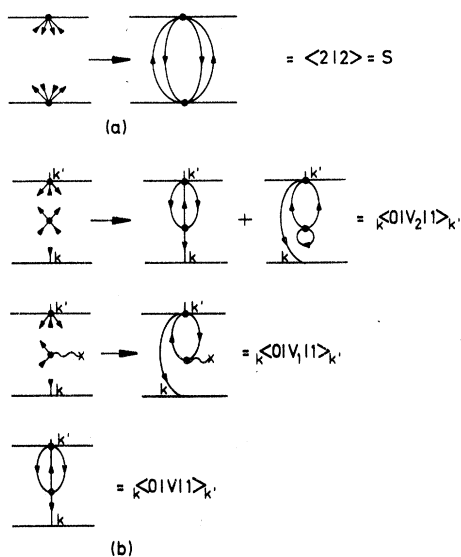


FIG. 2. (a) Skeleton  $\langle 2|:|2\rangle$  leads to only one diagram which is equal to  $S$  in Eq. (6). (b) Skeleton  $\langle {}_k\langle 0|:V_2:|1\rangle_k$  leads to two diagrams, where one of them is equal to  $-{}_k\langle 0|V_1|1\rangle_k$ . Thus  $\langle {}_k\langle 0|V|1\rangle_k$  contains only one diagram.

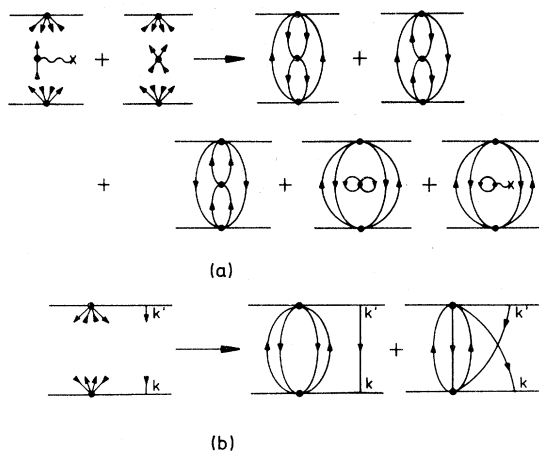


FIG. 3. (a) Sum of diagrams leading to  $\langle 2|V|2\rangle$ . The last two diagrams are each a product of two diagrams. The sum of these two diagrams is  $S(E_{HF} - E_{HF}^0)$ . (b) Sum of diagrams leading to  $\langle {}_k\langle 2|2\rangle_k$ . The first diagram is a product of two diagrams,  $S\delta_{kk'}$ .

the skeleton. All these possibilities lead to the same diagram. Another, more complicated, example is given in Fig. 2(b). The skeleton  $\langle {}_k\langle 0|:V_2:|1\rangle_k$  leads to two diagrams. The skeleton  $\langle {}_k\langle 0|:V_1:|1\rangle_k$  leads only to one diagram, which is equal, apart from the sign, to the second diagram of the first skeleton. Thus, only one diagram contributes to  $\langle {}_k\langle 0|V|1\rangle_k$ .

The skeletons shown in Fig. 2 lead to linked diagrams only. There are also examples where unlinked diagrams appear. As shown in Fig. 3(a), five diagrams contribute to  $\langle 2|V|2\rangle$ . The last two diagrams do not cancel as was the case in Fig. 2(b). It is a general rule that the diagrams due to  $V_2$  which contain a free line starting and ending at the same dot cancel the corresponding diagrams due to  $V_1$ . The only exception is when two free lines start and end at the same dot.

The rules for evaluating a given diagram are given in the following:

- (i) Multiply the elements appearing in a skeleton, leaving out the creation and destruction operators appearing in them as well as the factors in front of them, e.g., the factor  $\frac{1}{2}$  in  $V_2$ .
- (ii) Carry out the summation after inserting the Kronecker symbols according to the definition of the free lines in Fig. 1.
- (iii) Multiply the result obtained in (ii) by a factor  $2^{-q}(-1)^f$ , where  $q$  is the number of permutations of two equivalent free lines in the diagram leaving the diagram unchanged.  $f = f_1 + f_2$ , where  $f_1$  ( $f_2$ ) is the number of times free lines pointing downwards (upwards) cross each other.

As a consequence of the above rules the con-

tribution of an unlinked diagram is equal to the product of the contributions of the linked diagrams contained in it. Let us discuss four examples briefly. The overlap  $\langle 2|2\rangle$  is found with the above rules to be

$$S = \frac{1}{4} \sum_{\substack{i,j \leq N \\ m,n > N}} \frac{V_{mn[ji]}^2}{\mathcal{E}_{mni}^2}. \quad (\text{A3})$$

If we deal with a closed-shell system,  $S$  can be written as

$$S = \sum \frac{(2V_{mni} - V_{mij})V_{mni}}{\mathcal{E}_{mni}^2}, \quad (\text{A4})$$

where  $i, j$  are now doubly occupied and  $m, n$  empty orbitals. Analogously one finds the first diagram on the right-hand side of Fig. 3(b) to give a contribution  $S\delta_{kk'}$ . The sum of the two last diagrams in Fig. 3(a) gives  $S(E_{\text{HF}} - E_{\text{HF}}^0)$  and the last diagram in Fig. 2(b) leads to

$${}_k \langle 0 | V | 1 \rangle_{k'} = \frac{1}{2} \sum_{\substack{n > N \\ i,j \leq N}} \frac{V_{kn[ji]} V_{k'n[ji]}}{\mathcal{E}_{k'nji}}. \quad (\text{A5})$$

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