also indicate that in each of these instances the energy correction δE_c^e does not have an especially large effect on the estimate of the kinetic energy of the ejected electron. Consequently, the results given in Ref. 4 for the $\alpha\pi^- e^-$ and $\alpha K^- e^-$ atoms should be essentially unaffected, since the Auger rate for an energetically allowed transition from a circular orbit was shown there to be relatively insensitive to even fairly large changes in the kinetic energy of the ejected electron. However, in the case of the $\alpha\bar{p}e^-$ atom, the results shown in Fig. 1 indicate that it is likely that the values of $|\Delta n|_{\min}$ for the circular orbits with $n = 32$ and 35 are, respectively, 4 and 5 instead of 3 and 4.

The other reason for estimating $E_c - E_c^{dv}$ is to obtain corrections to the energy difference ϵ_c^{dv}. It has been noted[6] that a relatively large energy splitting inhibits the rate for Stark transitions between two states with the same principal quantum number and with angular momenta differing by one unit. In the instances that are listed in Table II, the corrections to ϵ_c^{dv} are only a few percent at most. Partly because of the relatively large change in linear momentum that probably must accompany an inelastic collision with a He atom during which an $\alpha\pi^- e^-$ or $\alpha K^- e^-$ atom loses orbital angular momentum, and partly because of a number of other uncertainties inherent in the methods of calculation presently available,[7] the corrections to ϵ_c^{dv} listed in Table II are therefore not large enough to cause any meaningful change in an estimate of the rate with which circular orbits of these particular principal levels can be depopulated by Stark mixing.

ACKNOWLEDGMENT

The author wishes to thank Professor B. Goodman for a helpful discussion.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 6 DECEMBER 1970

Many-Body Perturbation Theory for the Hydrogen Negative Ion*

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(Received 14 May 1970)

Linked-cluster many-body perturbation theory is applied to study the stability of the ground state of the H⁻ ion. A diagrammatic approach is made to analyze the role of various polarization effects. A complete set of states obtained in the V^{N-1} potential is used to evaluate the diagrams. The total energy of H⁻ is calculated to be − 0.027 66 a.u., leading to the binding energy 0.527 66 a.u., in good agreement with the most accurate value, 0.027 75 a.u., due to Pekeris. The result of our investigation shows conclusively the crucial importance of monopole and dipole polarization effects for the stability of this ion in particular and negative ions in general. A comparison with the results from earlier work is also made.

The binding energy of negative ions provides a good testing ground for the adequacy of many-body theory. The reason for this is that these ions are rather weakly bound, the binding energy being a small fraction of the total energy of the atom, similar to the situation of the dissociation energy in diatomic molecules. In most of the negative ions studied to date, Hartree-Fock theory is unable to explain the stability with respect to the ionization into the neutral atom and an electron.[1] For the H⁻ ion, which is the simplest example of a negative ion, Pekeris,[2] by his extension of Hylleraas's technique, has been able to demonstrate its stability. However, Pekeris's treatment utilizing the wave function involving r_{12} is too complicated to provide insight into the role of various types of correlation effects between the electrons, which could be generalized to heavier systems. In particular, the role of instantaneous polarization effects in contributing to the binding of ions has recently been questioned.[3] Using various approximations involving open-shell wave functions similar to those employed earlier by Löwdin and Shull,[4] Goddard[3] has shown that it is possible to obtain a part of the binding energy and has concluded that the instantaneous polarization effects are not "crucial" to the stability of H^-. On the other hand, Oberoi and Callaway,[5] in their recent variational calculation involving polarized orbitals, have been able to obtain a binding energy comparable to that of Pekeris.[2] However, it is difficult to assess the relative importance of various orders of polarization on the binding energy from their work because of the sensitivity of their results to the variational functions and various approximations they employed. To settle definitely the question of the role of polarization, it is therefore necessary to utilize an approach in which various types of polarization effects are handled explicitly. The Brueckner-Goldstone (BG) many-body perturbation theory[6,7] is such a procedure, where various physical correlation effects are represented by appropriate diagrams. In addition to this aim, the present work, being the first application of many-body perturbation theory to the study of negative ions, is also of considerable interest since it exhibits certain general features unique to loosely bound systems.

Since the BG many-body perturbation theory has been discussed at length several places in literature, only the barest essentials will be given here. The basic aim of many-body theories is to obtain the eigenfunctions and the eigenvalues of the total atomic Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} T_i + \sum_{i>j} 1/r_{ij} \ , \tag{1}$$

where T_i is the sum of the kinetic energy and nuclear attraction energy; N, being the number of electrons in the atom, is equal to 2 for H^-. In applying the perturbation approach, one utilizes a neighboring Hamiltonian $\mathcal{H}_0$ for which one can obtain a complete set of states. Using this basis set, the perturbation energy is evaluated to various orders in $\mathcal{H}' = \mathcal{H} - \mathcal{H}_0$ through the linked-cluster perturbation approach.[8] For an atom, a convenient choice of $\mathcal{H}_0$ is the Hartree-Fock Hamiltonian, the corresponding lowest eigenstate Φ_0 being the determinant composed of the N lowest solutions φ_n of the equation

$$(T+V)\varphi_n = \epsilon_n \varphi_n \ , \tag{2}$$

where V is the one-electron Hartree-Fock potential. It has been shown that one can obtain the actual energy E of the system from the zeroth-order energy E_0 defined by

$$\mathcal{H}_0 \Phi_0 = E_0 \Phi_0 \tag{3}$$

through the linked-cluster expansion

$$E = E_0 + \sum_n \langle \Phi_0 | \mathcal{H}'[(E_0 - \mathcal{H}_0)^{-1}\mathcal{H}']^n | \Phi_0 \rangle_L \ , \tag{4}$$

where the subscript L indicates that only linked diagrams have to be included in a diagrammatic expansion of E. From an experimental point of view, the important quantity for H^- is the electron affinity

$$A(H) = E(H) - E(H^-) \ , \tag{5}$$

$E(H)$ and $E(H^-)$ being the energies of the ground states of H atom and H^- ion. Atomic units (e^2/a_0) are used throughout this work. For the stability of H^- it is necessary that $A(H)$ be positive. The correlation energy for the ion is related to $A(H)$ through the equation

$$\begin{aligned} \Delta E_c &= E(H^-) - E_{HF}(H^-) \\ &= E(H) - A(H) - E_{HF}(H^-) \ , \end{aligned} \tag{6}$$

the Hartree-Fock energy $E_{HF}(H^-)$ being given as usual by the sum of E_0 and the first term in the summation in Eq. (4).

As in earlier calculations on bound states of atoms,[6,7] the V^{N-1} choice was utilized for the one-electron potential. In the present case, because we have only two electrons in a ^1S state, $V(r)$ reduces to the form

$$V(r) = \int d\vec{r}' \, |\varphi_{1s}(\vec{r}')|^2 / |\vec{r} - \vec{r}'| \ . \tag{7}$$

For the initial choice for φ_{1s} in Eq. (7), we utilized an analytic form for

$$\varphi_{1s} = N(e^{-\mu r} + c e^{-\lambda \mu r}) Y_{00}(\theta, \phi) \ , \tag{8}$$

obtained by Green *et al.*[9] Using this $V(r)$, φ_{1s} was obtained from Eq. (2) by numerical integration and iterated by the use of the calculated φ_{1s} in Eq. (7) for self-consistency. The final value obtained for ϵ_{1s} was -0.04592 a.u. as compared with Green's value of -0.04912 a.u. Using the calculated value of ϵ_{1s} and computing the Coulomb interaction energy between two electrons, one obtains the Hartree-Fock energy $E_{HF} = -0.48812$ a.u., which is larger than that of the hydrogen atom by 0.01188 a.u., indicating instability with respect to ionization. In contrast to neutral atoms, no bound excited states were found. This is because the V^{N-1} potential in the present case leads essentially to zero effective charge for large distances in the same way that the choice of V^N potential does for the neutral atoms. The radial components of the excited continuum functions with energy $\frac{1}{2}k^2$ are admixtures of Bessel and Neuman functions $j_l(kr)$ and $n_l(kr)$. Normalization was accomplished by noting that at large distances

$$R(kl;r) = A[\cos(kr + \delta_{l,k} - \tfrac{1}{2}(l+1)\pi)]/r \ . \tag{9}$$

The amplitude A was chosen to be unity in keeping with the convention for integration of the diagrams over k. The lowest-order contribution to the correlation energy is given by Fig. 1(a). This figure describes the mutual polarization of the two electrons

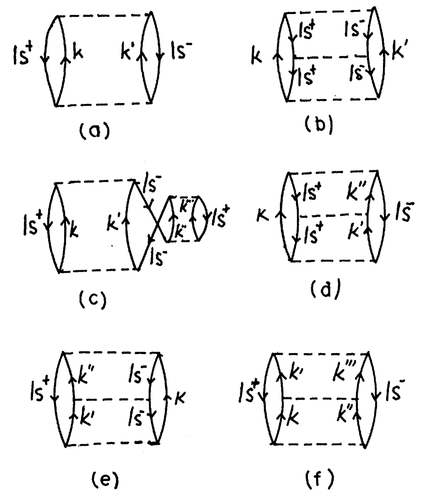

FIG. 1. Correlation-energy diagrams for H$^-$: (a) lowest-order diagram, (b) hole-hole interaction, (c) and its various time orderings, the rearrangement diagrams (d) and (e) hole-particle interactions and (f) particle-particle interaction.

in the ion. The contribution to the energy from multipole order l in the mutual polarization is given by

$$E_2^0(l)=\left(\frac{2}{\pi}\right)^2\int_0^\infty dk\int_0^\infty dk' \times\frac{\langle 1s1s|\,1/r_{12}\,|k_lk_l'\rangle\langle k_lk_l'\,|\,1/r_{12}\,|\,1s1s\rangle}{2\epsilon_{1s}-\epsilon_k-\epsilon_{k'}}\,. \tag{10}$$

Numerical integrations in k space in Eq. (10) were performed by a 12-point Gauss-Laguerre procedure, while in coordinate space Simpson's rule was utilized. The contributions from $l=0,1,2,3,4$ are shown in column 2 of Table I. From the observed convergence of these values with respect to l, contributions from higher multipoles are not expected to be more than 10^{-5} a.u. The monopole and dipole contributions in Table I are comparable in order with the former somewhat larger in magnitude. On combining the contribution from Fig. 1(a) with E_{HF}, the total energy up to this order is given by $E(\mathrm{H}^-)=-0.54261$ a.u., and $A(\mathrm{H})=0.04261$ a.u. Thus, while the correlation effects considered so far have explained the stability of H$^-$, they lead to an overcorrection, since presumably the most accurate value of $A(\mathrm{H})$ is 0.02775 a.u. This discrepancy can be resolved by a consideration of the higher-order diagrams in Figs. 1(b)–1(f). Figure 1(b) and its higher-order counterparts are the so-called hole-hole ladder diagrams. Figure 1(c) and its various time orderings are the rearrangement diagrams.[10] Figures 1(d) and 1(e) represent hole-particle ladders, and Fig. 1(f) represents particle-particle ladders. Of these, Figs. 1(b) and 1(c) can be shown to form a geometric series leading effectively to a change in the energy denominator in Fig. 1(a), namely,

$$D(\epsilon_k,\epsilon_{k'})=2\epsilon_{1s}-\epsilon_k-\epsilon_{k'}-\langle 1s\,1s\,|\,1/r_{12}\,|\,1s1s\rangle +\textstyle\sum_l E_2^0(l)\,. \tag{11}$$

Equation (10) is thus modified to

$$E_{2m}(l)=\left(\frac{2}{\pi}\right)^2\int_0^\infty dk\int_0^\infty dk' \times\frac{\langle 1s1s\,|\,1/r_{12}|k_lk_l'\rangle\langle k_lk_l'\,|\,1/r_{12}\,|\,1s1s\rangle}{D(\epsilon_k,\epsilon_{k'})}\,. \tag{12}$$

The third column in Table I thus represents the contribution to the correlation energy from various orders of l in Fig. 1(a), but corrected for diagrams of the types 1(b) and 1(c). The relative contributions from various l's are seen to have the same general features as those from Fig. 1(a), with $l=0$ making the numerically largest contribution. The corrections from these higher-order diagrams to the electron affinity and correlation energy are seen to be comparable to the respective quantities from the unmodified diagram in Fig. 1(a). This feature is a significant departure from the situation in neutral atoms and is a consequence of diffuseness of the negative-ion orbitals. The evaluation of hole-particle and particle-particle ladder diagrams is somewhat more involved, since they cannot be summed analytically. However, an examination of contributions from various orders of ladders indicates that a geometric series is a good approximation.[6] As a result one can express the sum of the contribution from the bare diagram in Fig. 1(a) and all the modifications in Figs. 1(b)–1(f) in the form

$$\Delta E_c=\textstyle\sum_l \Delta E_c(l)\,, \tag{13}$$

$$\Delta E_c(l)=E_{2m}(l)[1-2a(l)-t(l)]^{-1}, \tag{14}$$

where $a(l)$ and $t(l)$ are defined by

TABLE I. Correlation energy of H$^-$ (in a.u.).

l	$E_2(l)$	$E_{2m}(l)$	$E_c(l)$
0	−0.02811	−0.01952	−0.02043
1	−0.02202	−0.01532	−0.01582
2	−0.00330	−0.00230	−0.00239
3	−0.00097	−0.00071	−0.00064
4	−0.00009	−0.00007	−0.00006
Other[a]	···	···	−0.00020
Subtotal	−0.05449	−0.03792	−0.03954
	Hartree-Fock energy		−0.48812
	Total energy		−0.52766

[a] Contribution from the ladder-type diagrams with changes in l values of excited states.

TABLE II. Electron affinity of H (in a.u.).

Method	Results	Ref. no.
Polarized orbital	0.027 2	5
Goddard function	0.013 84	3
Split-orbital	0.013 3	4
C.I.	0.027 51	11
r_{12} coordinates (best value)	0.027 75	2
Present calculation	0.027 66	

$$a(l) = E_{3m}^{(h-p)}(l)/E_{2m}(l) , \tag{15}$$

$$t(l) = E_{3m}^{(p-p)}(l)/E_{2m}(l) . \tag{16}$$

In Eq. (15) $E_{3m}^{(h-p)}$ is the contribution from either Fig. 1(d) or 1(e). Similarly, in Eq. (16), $E_{3m}^{(p-p)}(l)$ represents the value of the modified diagram Fig. 1(f). The ratios $a(l)$ and $t(l)$ were evaluated by the usual approximation procedures for hole-particle and particle-particle ladder diagrams.[6] The values of $\Delta E_c(l)$ incorporating all the corrections are listed in the last column of Table I. Combining all the contributions, the net effect of hole-particle and particle-particle ladders obtained from the difference of the correlation energies in columns 4 and 3 of Table I is 0.001 62 a.u., which is smaller than the hole-hole ladder contribution but still sizable.

The results in Table I indicate clearly that s and p polarizations are both sizable and comparable to each other. Mutual polarizations of the d and f types are smaller but by no means negligible. Higher-order multipole polarizations are negligible in effect. In Table II we compare our results of the electron affinity with other calculations which were all done by variational procedures, and with Pekeris's results which are more reliable than the existing experimental data. The small difference of 0.000 09 a.u. between our result and Pekeris's is perhaps a result of the approximation procedure used in the evaluation of hole-particle and particle-particle ladders. In neutral atoms, the corresponding error is expected to be smaller because the orbitals are less deformable. The configuration interaction and polarized orbital results are in good agreement with ours. These calculations included various multipole polarization effects through the choices of the variational functions utilized. The reason for the smaller electron affinities obtained by Goddard and Löwdin and Shull is clearly due to their inclusion of only monopole polarization in their split-shell approach. The result of the present analysis indicates conclusively that polarization effects have important quantitative significance and have to be incorporated in variational calculations of energies and other properties, especially for negative ions. In the many-body perturbation procedure, these polarization effects are included naturally through the appropriate diagrams.

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*Supported by the National Science Foundation.

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