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Failure of the local exchange approximation in the evaluation of the H^- ground state

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The use of the local approximation for the exchange and correlation energy within the density-functional formalism has proven to be much more successful than originally anticipated. The calculation of the ground state for weakly bound negative ions, such as H^-, provides a sensitive test of the local approximation, which is known to lead to an incorrect asymptotic form of the single-particle effective potential. For H^-, the result is a qualitatively incorrect ground state, the electrons being partially delocalized. We show how this problem may be corrected by constraining the electrons with a fictitious spherical barrier at a large radius. For H^- we use this procedure to obtain a ground-state energy of -0.518 a.u. and an electronic affinity for H of -0.92 eV.

This paper presents a study of the ground state of the H^- ion within the local-density-functional theory[1,2] (LDFT); i.e., the exchange and correlation energy are included in a local approximation. The solution of this problem is of interest primarily for three reasons. First, several groups have recently used the LDFT to study the nonlinear screening of the proton in jellium.[3-5] In the limit of a low-density electron gas, one expects that system to tend toward H^- on physical grounds. Hence solving H^- within the same formalism may be useful in interpreting these results. The second reason is that the H^- calculation represents a very sensitive test of the local approximation for the exchange and correlation energy. Within the LDFT each electron feels a repulsive Coulomb potential from all of the electrons including itself. Coupled with the local approximation for the exchange energy, this leads to an incorrect form for the Hartree-like self-consistent potential. In particular, for singly charged negative ions, it leads to a spurious repulsive $+1/r$ potential far from the nucleus. Since H^- is weakly bound with respect to atomic H, the incorrect form of the effective potential might be expected to lead to difficulties in evaluating the ground-state properties. The final reason for examining the H^- system is that H is expected to be the simplest weakly bound negative ion which we might study. We expect that any difficulties in applying the LDFT to H^- will be reflected in attempts to solve other weakly bound negative ions in the same formalism.

When we applied the LDFT straightforwardly to H^-, we encountered certain subtle difficulties. In this paper we present a study of these difficulties, illustrating their origin and their connection to the local approximation for exchange. In addition, we discuss how a ground-state energy and density can be roughly extracted from our results.

The self-consistent H^- calculation was set up following the procedure of Tong and Sham[6] for atomic systems. As mentioned above, the exchange and correlation energy are included in a local approximation. In particular, we used the interpolation formula of Hedin and Lindqvist[7] to represent the bulk exchange and correlation energy. Initially several unsuccessful attempts were made to obtain the self-consistent solution for H^-. A common feature of the failures was that whenever the calculation was sufficiently close to self-consistency, the single-particle eigenvalue ϵ became positive. This corresponds to an unbound state and cannot be a self-consistent solution for the H^- energy functional since it implies that the effective potential is the bare nuclear potential, which however does have a bound state.

In order to investigate the apparent lack of a self-consistent solution for H^- within the LDFT, we considered a somewhat more general problem which includes H^- as a special case. In particular, we examined the self-consistent solution for the problem of two electrons moving in the field of a variable positive charge Z. For $Z=2$, this is just the LDFT calculation for He which is well known to have a straightforward self-consistent solution.[6] Our initial results therefore indicate that, for some intermediate value of Z between 1 and 2, the nature of the ground state changes. Self-consistent solutions were obtained for $Z>1.22$. In Fig. 1 we plot the values of both ϵ and the ground-state energy E as a function of Z. From the extrapolation of these solutions it can be seen that ϵ becomes positive for $Z<1.22$. The positive value of ϵ indicates a tendency on the part of the single-particle wave function to become delocalized. In order to further investigate the self-consistent result

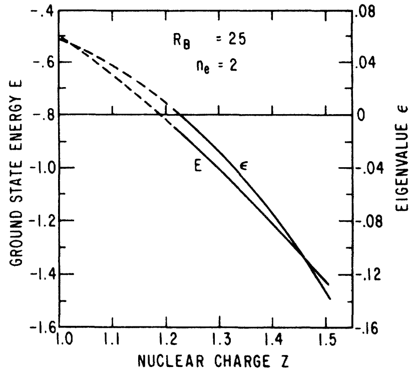

FIG. 1. Ground-state energy E, and single-particle eigenvalue ϵ, for variable Z. The dashed lines depend on the potential barrier at $R_B = 25$.

for $Z < 1.22$, we considered the solution of the H^- ion in a spherical potential barrier of radius $R_B = 25a_B$ ($a_B = 1$ Bohr orbit), by adding a fictitious external potential which is zero for $r < R_B$, and which is infinite for $r > R_B$. The result of these calculations is included in Fig. 1 by dotted lines for $Z < 1.22$. We find that ϵ is indeed positive, which indicates that the H^- density is being contained by the potential barrier. Hence the results for $Z < 1.22$ depend explicitly on the position of the barrier.

Since the barrier acts to confine the H^- density, it is of some interest to investigate the solution for H^- in wells of various radii. We obtained self-consistent solutions for box radii ranging from 7.5 to $75a_B$. In Fig. 2 we plot E and ϵ as a function of R_B. We see that for $R_B < 15a_B$ the energy depends sensitively on R_B. Between 15 and $30a_B$, there is a plateaulike region where the energy falls slowly as a function of R_B. For $R_B > 35a_B$, E falls rapidly up to the limits of our calculation. The various features of the energy versus barrier position curve can be explained by considering the single-particle effective potential, $v_{\mathrm{eff}}(r)$. For r close to the origin, $V_{\mathrm{eff}}(r)$ goes as $-1/r$. For R_B greater than about $10a_B$, v_{eff} rises to a maximum of 0.11 a.u. at $r = 8\ a_B$ and then falls off as $+1/r$ for larger distances. Finally the potential barrier at R_B causes $v_{\mathrm{eff}}(r)$ to rise to a large positive value. Thus we see that there are two potential wells for this $v_{\mathrm{eff}}(r)$. One is the Coulomb potential in the neighborhood of the proton. The other potential well lies between the maximum in $v_{\mathrm{eff}}(r)$ at $8a_B$ and the potential barrier. Since we are dealing with a positive ϵ, it is possible for there to be a zero-node solution for the single-particle wave function which has a large maximum near the proton and a secondary maximum in the second potential well near the barrier. For $R_B < 30a_B$, this secondary maximum does not appear in the self-consistent solutions, and the density remains exponentially localized on a scale of several Bohr radii. However, for $R_B > 30a_B$, a secondary maximum appears in the ground-state density corresponding to part of the electrons occupying the second potential well near the barrier. As R becomes larger, the amount of charge in the secondary maximum slowly increases. The solution with the barrier at $70a_B$ has approximately 0.2 electronic charges in the secondary density maximum. This charge lies in a low-density tail between $r = 40a_B$ and $70a_B$. We also note that the value of ϵ becomes less positive as R_B becomes larger.

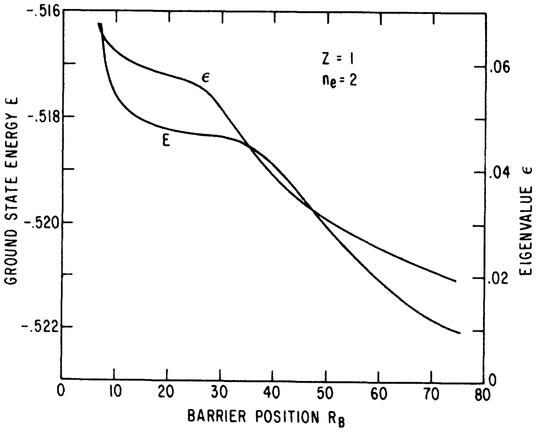

FIG. 2. Ground-state energy E, and single-particle eigenvalue ϵ, for H^- as a function of barrier position.

We now establish the ground-state solution for H^- as the box radius becomes infinite. Briefly, the result is that as R_B becomes large, the density in the core region tends to an asymptotic value which contains 1.7 electronic charges, and the ground-state energy of the system tends to a value of -0.526 a.u. The remaining 0.3 electronic charges are spread out in a low-density tail whose density falls off as $1/R_B^3$. The contribution of the tail region to the energy functional falls off as $1/R_B$. Hence in the limit of a very large box, the low-density tail gives a vanishingly small contribution to the energy.

In order to obtain this asymptotic solution for H^- as $R_B \to \infty$, we first note that finding the self-consistent solution is equivalent to varying the single-particle wave function to minimize the total energy. Then we consider the following class of wave functions. This class of wave functions contains n_e electronic charges ($n_e < 2$) within the core region ($r < 25a_B$) and $2 - n_e$ electrons in a tail of vanishingly small density. Since the low-density tail makes no contribution to the energy, we can vary the wave functions in the core region alone to determine the energy minimum for this class of wave functions. This is equivalent to solving the self-consistent equations subject to the constraint of having only n_e electrons in the core region. The self-consistent solutions were obtained for differing n_e within a box of radius $R_B = 25a_B$. The results for E and ϵ are shown in Fig. 3. For $n_e > 1.7$, the values of E and ϵ are drawn in with dashed lines since the solution for positive eigenvalues depends on the barrier position explicitly, as mentioned above. The most striking feature of the result is a minimum in the ground-state energy E for $n_e \simeq 1.7$. For the same value of n_e, the single-particle eigenvalue is zero. Since the solution for $n_e \simeq 1.7$ yields the absolute minimum in the energy, we conclude that this solution, with 1.7 electronic charges localized near the proton and 0.3 electrons spread throughout free space in a low-density tail, is the solution for H^- within the LDFT.

The zero value of ϵ for $n_e \simeq 1.7$ is consistent with the above conclusion. Consider H^- in a very large box. Then we notice that any single-particle potential which is close to the correct $v_{\text{eff}}(r)$ and for which $\epsilon < 1/R_B$ yields a density localized exponentially on a scale of several Bohr radii due to the $+1/r$ long-range tail. For values of ϵ greater than several times $1/R_B$, the wave function is completely delocalized within the box. For intermediate values of ϵ, we can find solutions with an arbitrary amount of charge localized near the proton. Hence as $R_B \to \infty$, we see that ϵ must tend to zero.

We have thus determined that the energy minimal solution for H^- within the LDFT has 1.7 electrons localized near the proton and 0.3 electrons delocalized throughout free space. Such a solution is clearly unphysical and arises as follows. The energy functional for the LDFT contains the interaction of an electron with itself in the evaluation of both the exchange energy and the electrostatic energy. The self-interaction terms would cancel in an exact evaluation. However, within the LDFT they are evaluated in different approximations. At large distances from the proton, the electrostatic self-interaction contributes a $+1/r$ tail to $v_{\text{eff}}(r)$. The local approximation for the exchange self-interaction on the other hand gives a contribution to $v_{\text{eff}}(r)$ which goes to zero exponentially at large distances. Thus we see that evaluating the exchange in the local approximation leads to an incorrect form for $v_{\text{eff}}(r)$. In particular, it is just the $+1/r$ term in $v_{\text{eff}}(r)$ which gives rise to the second potential well for the problem of H^- in a large box. This second potential well is the origin of the electronic delocalization as discussed above. Hence the local approximation for exchange leads directly to the incorrect partially delocalized ground state for H^- within the LDFT.

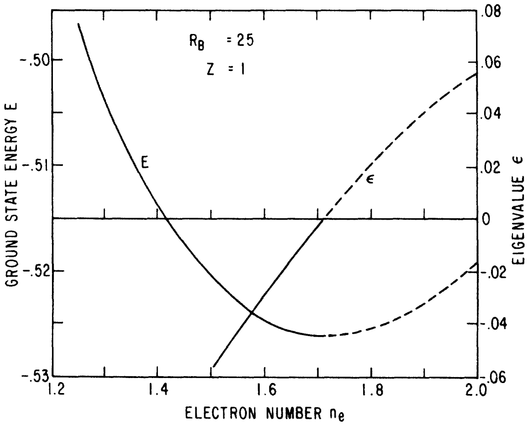

FIG. 3. Ground-state energy E, and single-particle eigenvalue ϵ, for H^- as a function of the number of electrons in core region n_e. The dashed lines depend explicitly on the potential barrier at $R_B = 25$.

Even though the energy minimal solution is clearly unphysical, we can roughly extract a "correct" solution for H^- from our results. From physical considerations we know that the H^- density is exponentially localized on a scale of several Bohr radii. Hence in the energy minimization, it would be reasonable to restrict oneself to the class of localized wavefunctions. In solving the problem of H^- in a box, we found that the electronic density remained localized on the proton for $R_B < 30a_B$. Solutions for box radii between 15 and $30a_B$ are found to have densities which are very similar in the core region and which differ only slightly in the exponential tail. Further, the energy for this region is roughly independent of box radius, as shown by the plateau region in Fig. 2. From the plateau region, we extract an energy of −0.581(4) a.u. as the ground-state energy of H^- A similar value for E has been obtained by Almbladh *et al.*[4] who evaluated the same energy functional as we used with the density obtained from a Hartree-Fock calculation.

Recently Gunnarson and Lundqvist[8] have reported an approximate energy for H^- within the LDFT of −0.529 a.u. They used an energy functional which includes spin as an independent variable, and they provided a parameterized form for the exchange and correlation which depends on the local spin density. Using the spin compensated (paramagnetic) limit of their energy functional, we found essentially the same phenomena for H^- as before, including a partially delocalized ground state. The plateau in the curve of E vs R yields a value of − 0.525(9) a.u. in rough agreement with their result; which they reported was somewhat uncertain due to convergence difficulties. The advantage of using the spin generalized version of the LDFT is that one can consistently calculate the ground states of H (net spin moment) and H^- (spin neutral). Gunnarson and Lundqvist reported the corresponding value for the ground-state energy of H was -13.4 eV. Using a slightly more accurate value (-13.38) we can subtract the H ground-state energy from that of H^- in order to obtain a value of -0.92 eV for the electronic affinity of H. This result should be compared with the results for a wave-function variation calculation using the exact Hamiltonian, which yields a value of -0.75 eV.[9] Thus we see that, although a naive use of the LDFT leads to both an unphysical ground state and energy, we can obtain relatively good answers for the H^- energy and the affinity of H by constraining the electrons with a spherical potential barrier at large radius.

In conclusion we discuss the consequences of our results for the problems introduced at the beginning of this paper. For the problem of the nonlinear screening of a proton in jellium, we conclude that the low density limit for that calculation would not be H^- but rather a solution with 1.7 electrons localized on the proton. However, since this would occur only for a $r_s \gtrsim 10$, it is not clear if our present results have any implication for the numerical results reported in those calculations. Since the difficulties in the H^- ground state results from the local exchange approximation, we expect that the H^- problem should serve as a useful testing ground for nonlocal corrections to the exchange and correlation energy. Finally, we note that the problems associated with the calculation could arise in the evaluation of other weakly bound negative ions within the LDFT. Such difficulties should be anticipated whenever the ionic affinity is much less than $1/R_0$, where R_0 is a radius characterizing the outer electrons of the ion.

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