Simplest doubly charged negative ion: Nonexistence of H^{2-} resonances

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Two independent types of *ab initio* calculations for three electrons in the field of a proton have been carried out. Neither calculation shows any evidence for the existence of a resonant state of H^{2-} contributing to e+H^- inelastic scattering, at energies above the three-electron escape threshold. One of the methods used is based on an eigenchannel R-matrix calculation carried out within a reaction volume of finite radius r_0, followed by an averaging procedure over r_0. A second method is based on a configuration-interaction study of the dependence of the $2s^2 2p\,^2P^o$ resonance on the nuclear charge Z. These calculations suggest that previous experimental and theoretical studies of this system were in erroneous agreement that two $^2P^o$ resonances exist in H^{2-} above the three-electron escape threshold. We also show that the earlier apparent agreement between experimental and theoretical resonance properties would violate unitarity of the collision matrix.

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I. INTRODUCTION

One of the most remarkable experimental results of the past 25 years was the observation by Walton, Peart, and Dolder [1] of two resonances in the collision e+H^- →H+e + e, at energies slightly above the threshold (14.35 eV) for complete breakup of the system into p+e+e+e. The two resonances were observed at incident electron energies of 14.5 eV and 17.2 eV, with widths near 1 eV and 0.4 eV, respectively. The experiment was interpreted as an observation of resonance states of the four-particle system H^{2-}. Stabilization calculations by Taylor and Thomas [2] determined two resonances of H^{2-}, at roughly the energies observed experimentally, and classified them as $2s^2 2p\,^2P^o$ and $2p^3\,^2P^o$.

In the face of this agreement between theory and experiment, it might be tempting to conclude that this is a solved atomic physics problem. There remain, however, a number of important issues to understand about this amazing result. It is first of all qualitatively surprising that three electrons can remain bound to a proton for an appreciable time, with so much Coulomb repulsion in the system, especially at sufficiently high energies to permit complete disintegration of the system.

Recalling that the outer electron in H^- is itself very weakly bound by only 0.75 eV, it is not surprising that H^{2-} has been proved by Lieb [3] to be unstable. Lieb's proof does not rule out short-lived resonances of H^{2-}, but Simon has published a "proof" [4] that resonances in any many-particle system experiencing only Coulombic forces cannot exist at energies above the threshold for complete disintegration of the system. Specifically, Simon's proof excludes the occurrence of "poles of the resolvent" in this energy range. This proof has been discussed in simplified form by Hunziker [5], and recapitulated by Ho [6]. Doolen [7] has suggested that Simon's proof may not totally exclude the possibility of some type of resonances in this energy range, e.g., owing to poles of the resolvent on different Riemann sheets of the complex energy plane. In any case, the disagreement between Simon's theorem and the experimental results of Ref. [1] (and the resonance calculation of Taylor and Thomas [2]) has not been resolved.

In the two decades since the work of Taylor and Thomas [2], theoretical capabilities for handling nonperturbative electron correlations have improved dramatically. The goal of the present study is to use some of these improved techniques in an attempt to predict whether or not there are any H^{2-} resonance states lying in the energy range above the triple electron escape threshold. Our major conclusion is that we find no evidence for triply excited resonance states of H^{2-} that might contribute to the scattering process $e + H^- \rightarrow H + e + e$ observed by Walton *et al.* [1].

Specifically, the calculations reported in this paper do not show resonances in the e+H^- →H+e+e cross section for the low partial waves $L = 0$–3, at energies up to ~ 19 eV. These calculations are much more sophisticated than any of the previous calculations for this system; however, even the current calculations involve approximations that seem very plausible to us but might not accurately describe the physics of H^{2-}. The H^{2-} system is tremendously complicated compared to other three electron systems (He^-, Li, Be^+,...), because the electron-electron repulsion is much more dominant in H^{2-}. The calculations presented in this paper do not absolutely rule out the existence of resonances in the e+H^- →H+e + e cross section; no finite size calculation can do that. However, we have considered the existence of these resonances from three completely different angles: an argument from unitarity of the S matrix, a direct calculation of the cross section for low partial waves, and estimates of the position of the $2s^2 2p$ state from elaborate stablization-type calculations. These different approaches all indicate that the resonances seen in the Walton, Peart, and Dolder experiment are not due to e+H^- → H+e + e processes.

II. ARGUMENTS FROM UNITARITY OF THE S MATRIX

Prior to attempting any detailed theoretical calculations for this difficult system, it is possible to point out one immediate discrepancy between the experimental cross section [1] and the calculation by Taylor and Thomas [2] that indicated the two resonances are of $^2P^o$ character. If this theoretical classification is correct, the modulation of the experimental resonance violates unitarity of the scattering matrix, a point that appears to have gone unnoticed until now. Assuming that the resonance occurs for one value of L only, the depth of modulation of the cross section must be bounded by $\sigma^L_{\max} \leq \pi(2L+1)/k^2 \approx 8.2a_0^2$ for the (purported) $L=1$ resonance at 14.5 eV. However, the absolute measurement of Peart and Dolder [1] (see Fig. 2 of this reference) gives a modulation depth for the cross section at the 14.5 eV resonance which is an order of magnitude larger, namely $\sigma_{\rm res} \approx 80a_0^2$. If the experimental cross section normalization is correct, this would require that the orbital angular momentum of the resonant state should be greater than $L \approx 14$, which seems rather implausible. The electrons in the H^{2-} system feel much stronger repulsion than in any other atomic system. High orbital angular momentum adds centrifugal repulsion to the system making it much less stable. The other resonance at 17.2 eV has a much smaller modulation of $\approx 20a_0^2$ which would give a minimum value of $L=4$. Again, we think it is unlikely that the resonance would have such high orbital angular momentum; the most promising configurations for $L=4$ are $[2s(3d^2)^1G]^2G$ and $[(2p^2)^1D3d]^2G$ and $(3d^3)\ ^2G$ (the initial state of the system is $[(1s^2)\ ^1S\varepsilon g]\ ^2G$). None of these configurations is promising because none couples strongly to the $1s^2\varepsilon g$ initial state and therefore cannot give maximum variation in the $L=4$ cross section. Moreover, each is probably much less stable than the $(2p^3)\ ^2P^o$ state which does not appear to exist in our calculations.

The above values reflect the minimum values of L for the resonances based solely on unitarity of the S matrix, or flux conservation. In fact the minimum plausible values of L that could cause the resonances of Peart and Dolder [1] are presumably larger still. For instance, the experimental resonances in the Peart and Dolder [1] experiment have somewhat of a window-type line shape which means the maximum variation in the cross section depends on the background value. [For example, in the calculations described in the next section, the total probability for $e(\ell=3)+H^- \rightarrow H+e+e$ near the experimental resonance energies is $P \sim 50\%$; a window type resonance in this partial wave could give a variation in the cross section of $\pi 7P/k^2 \sim 11a_0^2$ compared to $22a_0^2$ if the background probability were 100%.] Also, the variation depends strongly on the coupling between the $H^-1s^2+\varepsilon\ell$ initial state and the resonance having no $1s$ electrons; scattering from the initial state to the resonance state involves three electrons changing orbitals which is a low probability process since the $1/r_{ij}$ coupling can directly change only two electron orbitals. A conservative estimate of the size of these effects raises the estimated L value for each resonance by a factor of 2–5.

The arguments given above rest partially on the assumed validity of the experimental cross section normalization. Other considerations indicate that the normalization must be substantially correct. The experiments of Dance *et al.* [8] gave a maximum cross section in this energy range of $(180\pm 20)a_0^2$, while Tisone and Branscomb [9] measured a maximum of $(150\pm 10)a_0^2$ at slightly higher energy. Initial theoretical estimates were conducted using a straight Born approximation, which cannot be given much credence in this energy range owing to the neglect of the Coulomb repulsion at large distances. For instance, the early Born approximation calculation by Geltman [10] overestimated the cross section severely, giving a maximum near $(4\times 10^3)a_0^2$, but this calculation was later seen to be in error because it neglected to account for nonorthogonality of the zeroth-order initial and final state wave functions. A Bethe-Born calculation by McDowell and Williamson [11], incorporating a crude semiclassical correction for this Coulomb repulsion, maximizes around $160a_0^2$ as do the experiments (see Fig. 14 of Ref. [9]). However this agreement may be somewhat fortuitous, as a different approach by Rudge [12], that attempted to account for the initial state Coulomb repulsion approximately, found a cross section maximum at much higher energies of only $3a_0^2$.

In the face of such theoretical disagreement, it is desirable to carry out an independent estimate of the nonresonant electron detachment cross section. We have calculated Coulomb-Born cross sections neglecting exchange and only including the dipole term in the $1/r_{ij}$ interaction. The resulting cross section maximum of $\sim 40a_0^2$ in this energy range presumably *underestimates* the full Coulomb-Born cross section because we have not included the higher multipole terms in the $1/r_{ij}$ interaction which can be important since the scattering electron at 1 a.u. of velocity readily penetrates inside the H^- wave function. Since H^- is so weakly bound, virtually every penetration of the scattering electron inside the H^- wave function results in detachment. Based on the size of H^-, the geometric cross section for $e+H^- \rightarrow H+e+e$ is expected to be $\sim (\pi/2E_b)a_0^2 \sim 60a_0^2$ ($E_b \simeq 0.028$ is the binding energy of H^- in a.u.) since the relevant size for H^- is $1/\sqrt{2E_b}$.

The cross section bounds discussed above also rest on the assumption that each of the resonances arises in only one partial wave, L. Although extremely unlikely, there does not appear (at first) to be any reason why each observed resonance cannot result from the superposition of many resonances from different partial waves. However, the physics of the H^{2-} system argues against this already unlikely situation. An H^{2-} state would be extraordinarily floppy from the large amount of repulsion. A floppy system can be easily distorted when angular momentum is added to the system, and accordingly its lowest energy state should increase rapidly with increasing angular momentum. We doubt that H^{2-} has resonances for 5–10 different values of L within 1 eV of each other, which would appear to be necessary for the experimental resonance modulation at 14.5 eV to be correct.

III. DIRECT CALCULATION OF THE CROSS SECTION

A. Theoretical techniques

The H^{2-} system is hardly a trivial one to describe theoretically, even for methods that have successfully described other highly correlated systems like helium, H^-, the alkaline earth atoms [13,14], and various open-shell atoms [15]. A major reason for the complexity is the fact that in the energy range under consideration, multiple electron continua are present. A combination of eigenchannel R matrix and quantum defect methodologies has successfully treated autoionizing resonance states in energy ranges where the decay is restricted to single-electron escape only. Such energy ranges are now handled routinely, and typically with great success. In the present problem, however, the two-electron final state continuum $H(n = 1) + e + e$ becomes energetically allowed for incident electron energies larger than the 0.75 eV binding energy of the outer electron in H^-. At higher energies additional two-electron continua are also open, such as $H(n = 2) + e + e$ and so on. When the energy is increased still further, i.e., above the triple escape threshold at 14.35 eV incident electron energy, there are an infinite number of double-escape continua that are energetically open, and a triple-escape continuum as well. Currently, there is no theoretical method that correctly describes double or triple continua when correlations are important.

The theoretical techniques used in this study are primarily adapted from the eigenchannel R-matrix approach, with some extensions. In particular, our ability to approximately describe the effects of multiple electron escape continua improves substantially upon previous eigenchannel R-matrix calculations. The calculations are conducted within a sphere in real space, which takes the shape of a hypercube in the three-dimensional radial portion of configuration space, with $0 \le r_1 \le r_0$, $0 \le r_2 \le r_0$, $0 \le r_3 \le r_0$.

As in all previous eigenchannel R-matrix studies, we assume that beyond the surface of this radial hypercube, at most one electron can escape. In the next section we show how to approximate the cross section for $e+H^- \rightarrow H+e+e$ using wave functions for which only one electron can escape to distances larger than r_0. The eigenchannel R-matrix technique allows us to obtain a numerical approximation to the logarithmic derivative matrix (R matrix) for which the errors are of second order in errors of the wave function. We obtain the linearly independent wave functions by superposing orthonormal basis functions in a small region of space called the R-matrix volume. The relevant matrix equation for the superposition coefficients, in $\psi_{E\beta} = \sum_j y_j(\mathbf{r}) C_{j\beta}(E)$, is

$$\underline{\Gamma}\mathbf{C}_\beta = b_\beta \underline{\Lambda}\mathbf{C}_\beta \,, \tag{1}$$

where $\Gamma_{ij} = 2\langle y_i|E - H|y_j\rangle - \langle\langle y_i|\partial/\partial n|y_j\rangle\rangle$ and $\Lambda_{ij} = \langle\langle y_i|y_j\rangle\rangle$. As usual, each $y_j(\mathbf{r})$ represents one antisymmetrized, single configuration, three-electron basis function, coupled to a definite total L, S. The double bracket notation indicates integration only over the surface of the R-matrix volume, and the normal derivative of $\psi_{E\beta}$ at this surface is $\partial\psi_{E\beta}/\partial n = -b_\beta\psi_{E\beta}$. The matrix equation (1) is solved using the streamlined eigenchannel approach [16] to reduce the computer time needed to obtain the R-matrix at many different energies.

The initial state of the system is an H^- ion in its $^1S^e$ ground state with a continuum electron of orbital angular momentum ℓ; the total orbital angular momentum of the initial state is $L = \ell$ because the total orbital angular momentum of the two H^- electrons is zero. We can ignore the spin-orbit interaction for this system which means we only need to consider three electron wave functions whose spins are coupled to total spin 1/2 and whose parity is $\pi = (-1)^\ell$. In a more compact notation, the symmetry of the relevant three electron wave functions is $^2L^\pi$ where $\pi = (-1)^L$. To calculate the total cross section for $e+H^- \rightarrow H+e+e$ we would add the partial cross sections for $^2S^e$, $^2P^o$, $^2D^e$, $^2F^o$, ..., total symmetries, increasing L until convergence is achieved.

The basis functions for our variational R-matrix procedure are constructed from hydrogenic orbitals. The two electron core states were constructed by diagonalizing the two electron Hamiltonian with the basis $(1s^2)^1S$, $(2s^2)^1S$, $(1sns)^{1,3}S$ (with $n = 2$–7), $(2s3s)^{1,3}S$, $(2p^2)$ (^1S, ^3P, ^1D), $(2p3p)$ (^1S, ^3P, ^1D) for the even parity core states and $(1snp)^{1,3}P^o$ (with $n = 2$–7), $(2s2p)^{1,3}P^o$, and $(2s3p)^{1,3}P^o$ for the odd parity core states; all of the hydrogenic orbitals used for these basis functions are zero at r_0. The lowest core eigenstate gives the ground state of H^- with a binding energy $\sim 40\%$ smaller than the physical binding energy of H^-. All of the other eigenstates are at energies > -0.5 a.u. and give a discretized representation of the $H+e$ continuum and resonant states. The three electron wave functions of $^2L^\pi$ symmetry were obtained by adding orbitals of angular momentum $\ell = L$ onto the even parity core states and orbitals of angular momentum $\ell = L \pm 1$ onto the odd parity core states. For example, some of the basis functions for $^2F^o$ symmetry were $(1s2s)^3Snf$, $(1s2p)^1P^ond$, and $(2s2p)^3P^ong$. For the lowest partial waves, $L = 0$–3, all of the relevant correlation type basis functions were added; for example, for the $^2P^o$ symmetry, basis functions of the type $(2p^2)^1S2p$, $(2p^2)^3P2p$, and $(2p^2)^1D2p$ are not allowed separately but the one linear combination of these giving the $(2p^3)^2P^o$ state is allowed and was included in the calculation for $^2P^o$ symmetry.

The number of three electron basis functions increases dramatically as the number of two electron basis functions increases which is why the number of core basis functions is so small. We have made several tests of the convergence of the cross section with the size of the H^- basis functions. One crucial test was how well the $(1sns)^{1,3}S$ and $(1snp)^{1,3}P^o$ states discretized the continua. For $^2P^o$ symmetry, we found that decreasing the maximum value of n in the calculation from 7 to 6 changed the cross section by less than 5%. Since any resonance of H^{2-} will certainly have no $1s$ electrons, the small number of doubly excited H^- basis functions is a more serious concern. However, the cross section for the $^2P^o$ symmetry changed by less than 2% when we added the core basis functions $(3s^2)^1S$,

$(3p^2)$ $(^1S,\ ^3P,\ ^1D)$, $(2s4s)^{1,3}S$, $(2p4p)$ $(^1S,\ ^3P,\ ^1D)$, $(2s4p)^{1,3}P^o$, and $(3s3p)^{1,3}P^o$. Another concern was the small number of LS core symmetries included in the calculation. For example, there are no basis functions which discretize the $(1s\varepsilon d)^{1,3}D$ continua in H^-. The inclusion of basis functions of H^- that discretize this continuum would broaden any resonance in the calculation because it would give the resonance another decay channel and it would change the background value of the cross section due to (for example) the direct quadrupole interaction of this continuum with the ground state. Unfortunately, the direct inclusion of core basis functions of this symmetry increases the size of the three electron basis set by 50–70 %, and would stretch the capability of the workstation we used to calculate the cross section. [A large part of the effect of the $(1s\varepsilon d)$ continua is included in the $^2P^o$, $^2D^e$, and $^2F^o$ symmetries; for the odd parity symmetries there are basis functions of the type $(1snp)^{1,3}P^o n'd$ and for the $^2D^e$ symmetry there are basis functions of the type $(1sns)^{1,3}Sn'd$ in the R-matrix calculation which gives some representation of the $(1s\varepsilon d)^{1,3}D$ continua.] The final convergence problem concerns the $1s^2$ ground state of H^-. We obtain $\sim 60\%$ of the binding energy of H^- with the small basis set that we used. This means that our $1s^2$ wave function extends to distances farther from the nucleus and is easier to ionize than the physical $1s^2$ state of H^-; a larger $1s^2$ wave function also increases the probability for scattering from $1s^2\varepsilon\ell$ into highly correlated triply excited states like the $2s^22p$ state.

Once we have obtained the ψ_β from the variational R-matrix procedure, we can construct linear combinations of the ψ_β to obtain new linearly independent solutions that have the form

$$\psi_{E,i} = A\sum_j \phi_j(\Omega)[f_j(r)\delta_{ji} - g_j(r)K_{ji}] \qquad r > r_0\ , \quad (2)$$

where A is the antisymmetrization operator, $\phi_j(\Omega)$ contains all of the degrees of freedom except the radial motion of the outer electron, f_j and g_j are energy-normalized regular and irregular radial solutions for the repulsive Coulomb potential with charge -1, and $\underline{K}$ is the reaction or reactance matrix that contains the scattering information needed to obtain cross sections. The core eigenstates were obtained (as discussed above) by diagonalizing the H^- Hamiltonian in basis functions that are zero at r_0. The f and g were obtained by integrating Milne's equation for a repulsive Coulomb potential from large r into r_0 (see, e.g., Ref. [17]). In Eq. (2) the sum is only over channels such that the outer electron in channel j has positive kinetic energy at $r \to \infty$.

B. Total inelastic cross section

The calculation of the $e+H^- \to H+e+e$ cross section is not simple using the information contained in the wave function of Eq. (2). Remember, the outer electron moves beyond the hypercubic reaction volume in the field of a two-electron Hamiltonian eigenstate; this eigenstate is subject to the boundary conditions that its wavefunction vanishes on the reaction box surface. All but one of the two-electron "target" eigenstates included in this manner lie at energies in the one-electron continuum; H^- has only one bound state and we have not added any basis functions that represent the two electron continuum of H^-. The wave functions of Eq. (2) contain many terms where the core part of $\phi_j(\Omega)$ is a discretized continuum state of H^-; these channels are like a discretized double continuum of H^{2-} since the f and g are themselves continuum functions. Such a finite-volume representation has severe limitations *because* the "continuum energies" of the two-electron target system become quantized when calculated in a finite volume. It should be possible to similarly describe the three-electron escape continuum in this manner, but we have not included functions capable of representing such channels beyond the reaction volume.

In all that follows, channel $j = 1$ will be the channel representing the initial state of the system, namely $e(\ell) + H^-(1s^2)$. With the unphysical boundary conditions we have imposed on the wave function, we can calculate the total probability for inelastic scattering for any L using

$$P^L(r_0) = \sum_{j>1} |S^L_{1j}|^2\ , \quad (3)$$

where $\underline{S}^L = (\underline{1} + i\underline{K}^L)/(\underline{1} - i\underline{K}^L)$ is the S matrix for symmetry $^2L^\pi$. In Eq. (3), we have indicated explicitly that this probability depends on the unphysical boundary conditions we have applied at r_0. The $P^L(r_0)$ (for a fixed r_0) contains much of the information on the total probability, P^L, for $e(\ell)+H^- \to H+e+e$ because all of the excited channels, $j > 1$, represent discretized double electron continua. Note that the contribution of the Lth partial wave to the inelastic scattering cross section in a.u. can be obtained from P^L by using the formula $\sigma_{\rm inel} = \pi(2L+1)P^L/k^2$, where k is the wave number of the incident electron.

The introduction of a box with hard boundary conditions causes a type of "ringing" in our spectrum. In Fig. 1 we show (dashed line) the total probability for inelastic scattering for the $^2P^o$ symmetry (the solid line

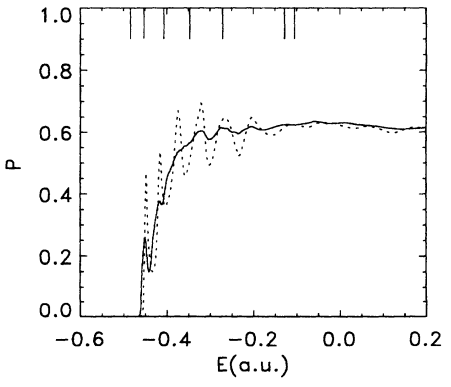

FIG. 1. The $^2P^o$ inelastic scattering probability (dashed line) for $r_0 = 25$ a.u. The vertical lines mark the energy positions of the two-electron $^3P^o$ target states. The solid line is the r_0 averaged $^2P^o$ inelastic scattering probability.

is discussed below) for a fixed r_0. At the top of the figure are vertical lines marking the positions of the $^3P^o$ target energies for this r_0. The most striking features of this curve are the large amplitude resonances in the double electron continuum of H^{2-}. These resonances are real for the boundary conditions that we have imposed on the system, but the boundary conditions are unphysical. The resonances occur when the incoming electron excites the H^- to a box state and loses most or all of its kinetic energy. This slow electron can enter a resonant state on the potential created by the excited H^- box state. This characteristic but unphysical ringing is immediately apparent in the calculation, but it can be eliminated to a very large extent by averaging the final spectra over the size r_0 of the reaction volume. Any physically observable resonance feature should stand out clearly by being insensitive to the value of r_0, provided the reaction volume is large enough to contain the bound portion of the resonance wave function.

We can approximate the physical total scattering probability, P^L, for $e(\ell)+H^- \rightarrow H+e+e$ as an average over the fixed-r_0 (unphysical) total inelastic scattering probability, $P^L(r_0)$. This idea of representing effects of double continua by a summation over discrete channels followed by some type of average has been used in diverse contexts [19], and it appears to give reasonable results in general. In this approximation, $P^L(r_0)$ is averaged over several values of r_0 to estimate the physical probability,

$$P^L \simeq \overline{P^L(r_0)}. \tag{4}$$

In Fig. 1, the solid line is the result obtained by averaging the $P^L(r_0)$ for $r_0 = 25$, 26, 27, 28, and 29 a.u. with equal weights. It is clear from this figure that all of the unphysical ringing discussed above is reduced greatly in amplitude for the averaged probability. This reduction occurs because these resonances are intimately associated with the box state thresholds of H^-; the energies of the box states of H^- that represent the different H^- continua decrease as r_0 increases which causes the resonances associated with them to decrease in energy. (The lowest energy unphysical resonance is still visible in the r_0 averaged probability because the lowest energy box state energy does not vary as much with r_0 as the higher energy box states.)

We have performed one test of this averaging procedure to verify that it can represent double continuum effects reasonably well. The test is a calculation of the $e-H$ elastic scattering cross section and the $e(E,\ell = 0)+H(1s) \rightarrow H(2s)+e(E',\ell = 0)$ inelastic scattering cross section at energies above the double-escape threshold. We have adopted the model Hamiltonian used by Temkin [21] and by Poet [20], which replaces $1/r_{12}$ by its scalar term only, $1/r_>$. When our calculation is performed in a fixed-r_0 R-matrix box, followed by averaging over r_0, the results agree well with the accurate results of Poet [20].

From Fig. 1 there do not appear to be any resonances in the $e(\ell = 1)+H^- \rightarrow H+e+e$ probability in the energy range of the experimental or theoretical resonances of previous workers. It is important to ask whether the averaging procedure discussed above might somehow reduce the effect of any physical resonances of H^{2-}. The answer to this question depends on the spatial extent of the resonance wave function. If a substantial portion of the resonant state extends to distances larger than r_0, then averaging over r_0 would cause the resonance to appear at too high an energy, possibly reducing its effect on the cross section as well. This is because the box boundary conditions constrain the resonant motion of the electrons. If the resonant state does not extend to distances larger than r_0, then the averaging procedure should not reduce the effect of the physical resonance because the box boundary conditions would only affect the continuum part of the wave function; the physical resonance energy would not shift by amounts more than its physical width and, in fact, this small shifting correctly contributes to the physical width since the width for a fixed r_0 is usually too small. It does not seem plausible that any physical resonance above the triple continuum threshold of H^{2-} would extend to distances larger than 25 a.u. because any resonance of this system should represent highly correlated motion with all electrons near the same distance from the proton. When the electrons reach this distance they can simply continue outward to infinity; there are no barriers in the potential at these distances that can give reflection and contribute to resonant motion.

C. Results

The total $^2P^o$ scattering probability (solid line) for $e(\ell = 1)+H^- \rightarrow H+e+e$ shown in Fig. 1 contradicts the earlier interpretation that the H^{2-} experimental resonances have $^2P^o$ symmetry. In this figure, there is no evidence for any physical resonance near zero total energy. The results presented in Fig. 1 are from a calculation many times larger than the original theoretical work [2] on the H^{2-} resonances. We have therefore performed test calculations using drastically reduced basis sets to explore the connection between the current elaborate calculations and the previous theoretical work.

In Fig. 2, we present the total inelastic scattering probability (solid line) and the trace of Smith's [18] time delay matrix (dashed line) for a *small, unconverged calculation* with a box of 25 a.u. The channels included in the calculation were $(1s^2)^1S\varepsilon p$, $(2s^2)^1S\varepsilon p$, $(1s2s)^{1,3}S\varepsilon p$, $(1s2p)^{1,3}P^o\varepsilon s$, and $(1s2p)^{1,3}P^o\varepsilon d$; the states $(2p^3)^2P^o$ and $(2p^2)^1S3p$ were also included. The time delay is flat except near the $2s^22p$ resonance at ~ -0.05 a.u. and near the $2p^3$ resonance at ~ 0.1 a.u. (Note that already in this small basis set the $2s^22p$ resonance is *below* the $p+e+e+e$ threshold.) The $2p^3$ resonance produces a distinct Fano profile in the total inelastic scattering probability whereas the $2s^22p$ resonance has very little effect. The $2p^3$ resonance completely disappears when the $(2p^2)$ $(^1S,\ ^3P,\ ^1D)\varepsilon p$ channels are added to the calculation. The full calculation does not show either of these resonances in the inelastic scattering probability which means they cannot be seen in the previous electron scattering experiments. Laying aside the question of exciting these resonances, it is difficult to ascertain from the time

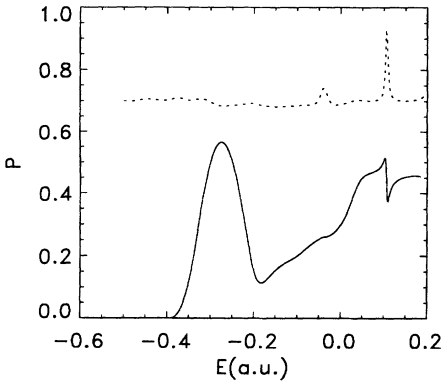

FIG. 2. This figure presents the results of a very limited calculation that has been deliberately truncated short of convergence. The dashed line is proportional to the trace of the delay-time matrix (shifted by 0.7) showing the $2s^2 2p$ and $2p^3$ $^2P^o$ resonances at ~ -0.05 and ~ 0.1 a.u., respectively. The solid line is the inelastic scattering probability which shows practically no structure near the $2s^2 2p$ resonance.

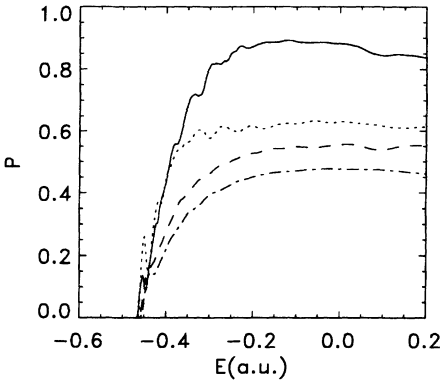

FIG. 3. The averaged inelastic scattering probability for $^2S^e$ (solid line), $^2P^o$ (dotted line), $^2D^e$ (dashed line), and $^2F^o$ (dot-dashed line) symmetries.

delay whether the resonances exist at all because the unphysical ringing obscures their existence; if they exist they are extremely broad. There is slight evidence in the larger calculation for a weak $2s^2 2p$ resonance at negative total energy, i.e., below the triple escape threshold.

Further evidence supporting our conclusion that a $2s^2 2p$ resonance (if it exists at all) should not show up strongly in the $e+H^- \rightarrow H+e+e$ scattering cross section can be found in the observed strength of a He^- triply excited resonance with the same label. In a measurement by Quéméner *et al.* [22], this resonance was observed at 57.2 eV incident electron energy in the analogous reaction $e+He \rightarrow He^+ + e + e$, but it causes only a 0.8% modulation of the cross section. For comparison, the modulation caused by the purported $2s^2 2p$ resonance in the $e-H^-$ experiment of Walton *et al.* [1] was approximately 50%, a huge qualitative difference from the He^- resonance that would be difficult to interpret. If anything, we would expect that a $2s^2 2p$ resonance in H^{2-} would be *less prominent* in the $e+H^-$ cross section because the resonance must be so much more diffuse if it exists in H^{2-}.

The $2s^2 2p$ and $2p^3$ resonances appear clearly in the small calculation because the artificially small number of angular couplings included in the basis set constrains the motion of the electrons unphysically. The number of decay paths is drastically reduced in the small calculation which can create resonant motion or greatly increase the lifetime of physical resonances. As the number of decay paths included in the calculation increases, the resonances broaden to the point where it is questionable if they exist. We speculate that the earlier calculation of Taylor and Thomas [2] was nearer to our "small" calculation, and may have obtained unconverged resonances similar to those in Fig. 2.

In Fig. 3, we show the total probability for inelastic scattering for the $^2S^e$, $^2P^o$, $^2D^e$, and $^2F^o$ symmetries. None of these curves show resonant structures near the energies seen experimentally. These symmetries are those most likely for resonant structure in the $e+H^- \rightarrow H+e+e$ cross section. An important property of these probabilities is that only the s-wave probability is ~ 1 and they are decreasing as L increases. This supports the arguments of the preceding section that the estimated bounds on L needed to explain the experiment, based on the unitarity argument, should be increased by a factor ≥ 2.

We have not calculated the scattering cross sections for higher L because we do not believe there can be any substantial resonances in that region of phase space when there are *none* for lower L. There are two reasons for this belief. The first is that the greater centrifugal repulsion for any proposed higher L resonance would tear apart this already unstable system. The second is that the $1/r_{ij}$ interaction that couples the $1s^2\varepsilon\ell$ initial state to the resonance state can only change the orbitals of two electrons at one time; however, the $1sn\ell n'\ell'$ states of H^{2-} are completely unstable. The only possible high L resonances have character $n\ell n'\ell' n''\ell''$ (where none of the orbitals are $1s$) but these states are not strongly coupled to the $1s^2\varepsilon\ell$ initial state and therefore cannot appear as strong resonances in the cross section. The size of an inelastic scattering resonance is proportional to the square of the coupling between the resonance and the initial channel, and is inversely proportional to the total width. High L resonances would have a very small branching ratio to the $1s^2\varepsilon\ell$ continuum because they are not coupled directly through the $1/r_{12}$ interaction; therefore we do not expect them to appear in high partial wave ionization cross sections.

IV. Z-DEPENDENT CALCULATION

In this section we examine the dependence of the $2s^2 2p\ ^2P^o$ resonance on nuclear charge Z, to show that the resonance given this label by Taylor and Thomas cannot correlate sensibly with the well-established analogous resonances for Li and He^-. The nuclear charge is treated as a continuous parameter in the range from $Z = 3$ (Li) to $Z = 1$ (H^{2-}), and we have calculated the position of the $2s^2 2p\ ^2P^o$ triply excited resonance state, for a given nuclear charge, by treating it like a bound state. The eigenenergies for the three electron system are calculated at a fixed Z by diagonalizing the three electron Hamiltonian matrix within a radial hypercube of side r_0. The basis functions used in calculating the matrix elements

of the Hamiltonian are similar to those used in the R-matrix calculation of Sec. III A; however, here we have included many more radial and angular configurations. The three electron basis functions are constructed from hydrogenic orbitals of charge Z that vanish at r_0. We have chosen $r_0 = 60/Z$ a.u., to take into account the fact that the mean radius for hydrogenic orbitals scales like $1/Z$. The two electron core states included in the calculation are $(ns^2)^1S$ (with $n = 2$–4), $(nsn's)^{1,3}S$ (with $n = 2$–$3, n' = 2$–4), $(nsn'p)^{1,3}P^o$ (with $n = 2$–$4, n' = 2$–4), $(np^2)^1S\ ^3P\ ^1D$ (with $n = 2$–4), $(npn'p)^{1,3}S\ ^{1,3}P\ ^{1,3}D$ (with $n = 2$–$3, n' = 2$–4), $(npn'd)^{1,3}P\ ^{1,3}D\ ^{1,3}F$ (with $n = 2$–$4, n' = 2$–4). We have omitted all $1s$ orbitals from the calculation. Three electron basis functions of symmetry $^2P^o$ were constructed from these two electron core states by adding orbitals of angular momentum l, consistent with the total angular momentum $L = 1$ and parity $\pi = -1$. The total number of three electron basis functions was approximately 650.

In Fig. 4, we show the present calculation of the eigenvalues of the three electron Hamiltonian (dots) as a function of the nuclear charge Z. The energy scale gives the $^2P^o$ eigenenergies relative to the $(2s^2)^1S$ energy for each Z, divided by Z^2. This energy scale gives the "binding" energy of the outer $2p$ electron relative to the $(2s^2)^1S$ two electron threshold ($E = -0.148$ a.u. for H^-). The asterisks are the energies calculated by Ahmed and Lipsky [23] for integer nuclear charge.

For $Z = 2, 3$ the lowest calculated box energy agrees well with the $2s^22p$ energy values calculated by Ahmed and Lipsky [23], Chung [24], Nicolaides [25], and others. However, for $Z < 2$ the position of the "resonance" is unknown. Our calculation is no longer as straightforward to interpret in this range because no single eigenstate obtained in the diagonalization can be unambiguously identified as "$2s^22p$." The basic problem for $Z < 2$ is that the $2s^22p$ resonance character is now distributed among numerous energy eigenvalues, many of which amount to a discretized representation of the continua such as $H^-(2s^2) + e(\varepsilon p)$. We have attempted to estimate the Z-dependent "resonance energy" for $Z < 2$ by examining the eigenvectors of the three electron Hamiltonian. In Fig. 4 we display the estimated position and width of this "resonance" as a function of Z, for $Z < 2$. These were determined by taking the overlap of the eigenvectors of the Hamiltonian at a given Z with the $Z = 2$ $2s^22p\ ^2P^o$ eigenvector. For $Z = 1$ we estimate a position of $E = -0.088$ a.u. and a width of $\Gamma \approx 0.04$ a.u. This energy is not in agreement with the calculation of Ref. [2], where an energy position of $E = 0.017$ a.u. was predicted for the $2s^22p\ ^2P^o$ resonance. We suspect our energy value is closer to being converged than that of Ref. [2], because our configuration-interaction basis set is about one order of magnitude larger, and also because our resonance energy correlates more naturally with the resonances classified as $2s^22p$ for Z in the range of 2–3.

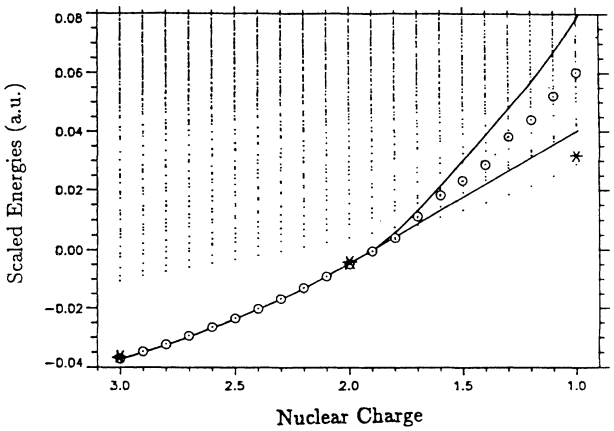

FIG. 4. Calculated eigenvalues of the three-electron Hamiltonian (dots) as a function of the nuclear charge Z. The scaled energies are shown relative to the $2s^2\ ^1S$ resonance energy at each Z, divided by Z^2. For $Z \geq 2$ the circled eigenvalues correspond uniquely to the energy of the $2s^22p$ state. For $Z < 2$ the circled eigenvalues were determined by taking the overlap of the eigenvectors at each Z with the $Z = 2$ $2s^22p$ eigenvector, and finding the maximum of the overlap distribution. The solid lines indicate the approximate width of the overlap distribution. The asterisks are the scaled $2s^22p\ ^2P^o$ energies calculated by Ahmed and Lipsky [22]. The lower of the two experimental H^{--} resonances [1] lies at a scaled energy of 0.15 a.u. for $Z = 1$.

It should be stressed that the $2s^22p\ ^2P^o$ resonance energy predicted in this section is below the total breakup energy for the system, and therefore does not contradict the "proof" of Ref. [4]. In fact this Z-dependent analysis cannot conclusively predict whether this resonance will really be observable in any experiment relating to $e-H^-$ scattering. For one thing, our R-matrix calculations suggest that excitation of any triply excited H^{2-} resonance from an electron collision with the H^- ground state is relatively improbable (even if the resonance exists), and so it would have comparatively little influence on the scattering cross section as in the $e-$He experiments of Ref. [22]. We do not regard this bound-state-type calculation as being able to definitively ascertain whether the $2s^22p$ state that we obtain for $Z = 1$ will be sufficiently long lived to be called a true "resonance." Nevertheless, the main conclusion to be drawn from the calculations of this section is clear: continuity in Z of the resonance position makes it improbable that any H^{2-} resonance above the triple detachment threshold $E = 0$ can be meaningfully identified as $2s^22p$.

V. CONCLUSIONS

We find ourselves in the admittedly awkward position of claiming that there are no H^{2-} resonances above the triple-escape threshold, a result that contradicts squarely with earlier experimental [1] and theoretical [2] efforts. While our initial goal was to calculate and better characterize the properties of these resonances, we have been unable to find them. We have confidence in the methods and approximations used in the present calculations, as they are natural extensions of techniques that have had widespread success in other contexts.

We find no alternative but to conclude that the experimental resonances observed at 14.5 eV and 17.2 eV by Walton, Peart, and Dolder [1] must not correspond to the H^{2-} system. It is hard to understand why the Ref. [1]

experiments would have seen artificial resonances corresponding to some other physical process, particularly considering the fact that the experiments were carried out by the same group using two different beam configurations. It seems relevant to note, however, that the same apparatus used to perform the $e+H^-$ scattering experiments was also used by Peart *et al.* [26] to measure $p+H^-$ neutralization cross sections. It is relevant because the neutralization measurements of Ref. [26] were eventually found to be erroneous; among other discrepancies this neutralization experiment found a resonance-type feature that eventually "disappeared" when further experiments were conducted by the same group and by other groups. A thorough and frank discussion of this whole matter has been presented by Dolder and Peart [27]. They conclude that the origin of this spurious resonance in $p+H^-$ neutralization collisions remains unknown to this day. Without knowing what caused this erroneous resonance to appear, we have no grounds to speculate whether or not the same mechanism might have caused the appearance of the two resonances in $e-H^-$ collisions. But clearly it will be highly desirable to see an independent experimental measurement. Apparently none has been conducted since the work of Ref. [1].

Another peculiarity about our conclusion that no triply excited resonances exist in H^{2-} is the resulting disagreement with the calculations of Taylor and Thomas [2]. We have only one possible reason for their (apparently incorrect and fortuitous) observation of two H^{2-} resonances in their stabilization calculation: we were able to see similar resonance features in our $e-H^-$ calculations performed with a very small, unconverged basis set. The calculations of Ref. [2] were very small compared to the current state of the art in configuration-interaction calculations. For instance, it included only s,p orbitals, whereas we have included far more s,p orbitals as well as d orbitals in our $^2P^o$ calculations. While our "small" calculation shown in Fig. 2 showed signs of similar resonances, these disappeared rapidly when the basis set size was increased, as discussed in Sec. III. The Z-dependent calculation of Sec. IV shows, at the very least, that if a $^2P^o$ resonance does exist near 14.5 eV, it should not be classified as $2s^22p$. Moreover, the experimental and theoretical results of Refs. [1,2], that are apparently in agreement, would violate flux conservation (or unitarity of the collision matrix).

On the other hand, our interpretation that there are no resonance states of H^{2-} above the triple-escape threshold would remove the disagreement between Refs. [1,2] and Simon's theorem [4] stating that no H^{2-} resonances can ever occur in this energy range. It might also be mentioned that some unpublished theoretical studies of H^{2-} $^2P^o$ symmetry failed to observe resonances above threshold. One of these was carried out by Chung [28], whose calculations seem particularly solid since the same type of calculations gave the He^- $2s^22p$ resonance position in excellent agreement with experiment. Another unpublished study was a calculation of H^{2-} hyperspherical potential curves by Greene and Clark [29]. These $^2P^o$ potential curves were unconverged but they also failed to show any signs of a shape-resonance-type feature that might be attributable to a $2s^22p$ or $2p^3$ resonance. It might also be mentioned that Beck and Nicolaides [30] performed a computational search for a $2p^3$ $^4S^o$ state of H^{2-} in an attempt to see whether such a state might be bound in LS coupling, to possibly explain a reported observation of H^{2-} in a mass spectrometer [31]. They found that this state is not bound, and that it lies around -0.09 a.u. relative to the triple-escape threshold, but they could not calculate the decay width to see whether it would survive long enough to be a resonance. In any case this $^4S^o$ resonance is irrelevant to electron scattering from the H^- ground state, as $^4S^o$ symmetry does not contribute to this process. A last H^{2-} calculation worth mentioning is a very small single channel close-coupling-type calculation for $^2P^o$ symmetry carried out by Temkin *et al.* [32]. This calculation included only one H^- target state, namely the $2p^2$ $^3P^e$, which was represented by a single-configuration product of Slater orbitals. The calculated $^2P^o$ p-wave scattering phase shift showed a broad ($\Gamma \approx 2$ eV) resonance whose center was barely above the triple-escape threshold, which Ref. [32] apparently interpreted as a $2p^3$ $^2P^o$ resonance. This calculation is again so limited in terms of radial and orbital configurations that we feel the calculated resonance is not likely to be real.

If our interpretation is correct that the experiments of Ref. [1] did not observe H^{2-} resonances, then it appears that no resonances nor bound states have ever been observed for *any* doubly charged atomic negative ion. Compton [31] has reviewed several reported observations of doubly charged atomic negative ions, but each such observation has apparently been reinterpreted otherwise. We speculate that some atoms may have doubly charged negative ion resonances, the best candidates being atoms with two holes in the valence shell such as oxygen and sulfur. In fact it is a simple and straightforward exercise to plot the binding energy of the outermost electron in the np^6 $^1S_0$ ground state along the neon isoelectronic sequence, i.e., for Si^{4+}, Al^{3+}, Mg^{++}, Na^+, Ne, F^-. These binding energies evolve in a smooth and simple way from one atom to the next, and a polynomial fit to these energies can be used to extrapolate an estimated resonance energy for O^{2-} in the $1s^22s^22p^6$ $^1S_0$ state. Our estimate for the resonance energy based on this extrapolation for O^{2-} is 7.2 eV above the O^- ground state. A similar extrapolation for S^{2-} predicts a resonance in $e-S^-$ scattering at 4.7 eV incident energy. These will presumably be very broad shape resonances, with widths greater than 1 eV. A different analysis by Herrick and Stillinger [33] predicts that the scattering resonance energy for O^{2-} will be $E = 5.38$ eV with a width of $\Gamma = 1.3$ eV, an energy somewhat lower than our extrapolated value. Gadzuk and Clark [34] estimate a higher energy $E = 8.8$ eV for the O^{2-} resonance. Huzinaga and Hart-Davis [35], on the other hand, predict values closer to ours, namely E=7.68 eV and E=4.62 eV for O^{2-} and S^{2-}, respectively, using a restricted Hartree-Fock-Roothaan approximation. Note that these doubly charged resonance states are well below the threshold energy for escape of all electrons to infinity, and therefore they would not be in violation of Simon's theorem [4]. More detailed experimental and theoretical tests are desirable to ascertain whether these unusual

doubly charged atomic negative ion resonances exist, and whether they have observable consequences.

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