

Perturbation Treatment of Hartree-Fock Equations for Resonance States of Three Electron Atoms and Ions

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A perturbation treatment of the Hartree-Fock equations using the inverse nuclear charge as perturbation parameter has been applied to several quasibound and metastable states of three-electron atoms and ions. The deviations of the results from the experimental values are discussed. The method should be particularly useful for heavier atoms and ions.

Eine störungstheoretische Behandlung der Hartree-Fock-Gleichungen, bei der die inverse Kernladung als Störungsparameter benutzt wird, wird für verschiedene quasibindende und metastabile Zustände von Atomen und Ionen mit drei Elektronen durchgeführt. Die Abweichung von den experimentellen Werten wird diskutiert. Die Methode sollte besonders für schwerere Atome und Ionen nützlich sein.

Introduction

Much theoretical work has been done to solve the Schrödinger equations of compound atoms such as H^- , He^- , Li^- etc., in the resonance energy range. Generally these resonance states lie in the continuum energy spectrum of the target system and so are not bound states. Rather, the wave function describing these states can be termed a localized wave packet with a lifetime of $\sim 10^{-14}$ sec. Since these states lie above an infinite number of lower states of the same symmetry, difficulties arise in applying the known approximations for bound states to resonance states. Thus, while for bound states these methods are more or less rigorous, for resonance states they are more empirical and therefore less predictive. It is convenient to discuss the problems arising in variational methods and perturbational methods separately.

Variational Methods

According to the variational principle, optimization of

$$E = \frac{\langle \psi_{tr} | H | \psi_{tr} \rangle}{\langle \psi_{tr} | \psi_{tr} \rangle}$$

gives an upper bound to the energy of the given state, but only when ψ_{tr} is orthogonal to all exact lower states. Thus, for resonance states, orthogonalization to ∞ states is necessary, i.e., using the Rayleigh-Ritz, method a secular equation of infinite dimensions must be solved. Using the HF method, the minimum of $\frac{\langle \psi_{HF} | H | \psi_{HF} \rangle}{\langle \psi_{HF} | \psi_{HF} \rangle}$ is found by varying the one electron functions, but again, one

must add the condition that ψ_{HF} is orthogonal to the exact lower states, get the corresponding integro-differential equations and solve them. This cannot be done, which means that even the HF approximation for the exact Hamiltonian of resonance states is not feasible.

Perturbation Techniques

One way of using such methods is to take the unperturbed Hamiltonian as $H = \sum_i A_i + \frac{1}{r_i}$ and $H' = \frac{1}{Z} \sum_{i \neq j} \frac{1}{r_{ij}}$. ψ_0 is chosen as the hydrogenic wave function of the given state. This gives E_0 and E_1 exactly even for resonance states, but problems arise for higher terms in the expansion of the energy or the wave function. To get the first-order wave function, the first order wave equation must be solved. As the perturbation is taken to be $\frac{1}{Z} \sum_{i \neq j} \frac{1}{r_{ij}}$, no exact solutions are obtainable. Therefore, variational solutions are tried and to ensure rigorous application of the Hylleraas conditions the lower states are to be taken into account, and $\psi_{1\text{tr}}$ must be chosen properly. If the orthogonality conditions are not observed, variation will give only the extremum of E_2 rather than the upper bound. However, in this case, by taking the exact zero-order wave-function, the exact E_0 and E_1 of the resonance state are obtained, and, in addition, the E_2 and E_3 obtained from ill-chosen $\psi_{1\text{tr}}$ will not be poor because the Hylleraas functional is dependent on ψ_0 .

Treatment of the Resonance States

The exact Hamiltonian of the compound atom in a resonance state is $H = \sum h_i + \frac{1}{Z} \sum_{i \neq j} \frac{1}{r_{ij}}$. The above should have made it clear that the eigenstate and eigenvalue of this Hamiltonian for resonance states cannot be found rigorously by known approximation methods (as they can for bound states). However, as shown by Fano [1], resonance states are found in the vicinity of bound states of the unperturbed Hamiltonian H_0 . This H_0 is part of the total Hamiltonian and must be chosen so that it does not contain terms causing interaction between the bound states and continuum states of H_0 . The remaining part, H' , expresses the interaction of bound and continuum states which physically gives rise to autoionization. Thus, part of the interelectronic interaction $\sum \frac{1}{r_{ij}}$ is included in H_0 , and the remainder leads to autoionization (or resonance). A proper choice of H_0 and H' is one that will give good agreement between the calculated lifetime of a resonance state (or resonance peak width) and the experimental value.

After an appropriate (and convenient) H_0 is found, approximation methods can be applied rigorously to find the states of H_0 and this gives the resonance energies. In order to find the width and shape of the resonance peak, the continuum states of H_0 must be obtained and the interaction elements of the matrices through H' must be calculated [1]. The choice of H_0 is not unique and is mostly

empirical, in contrast to the case of bound excited states where H_0 is always the Hamiltonian of the system without the electronic interaction. Only comparison with experiment will show whether H_0 was correctly chosen.

To summarize, the main problem in calculating resonance states is to find a good H_0 for the given state. From there on, the procedure is purely computational just as for bound states.

The problem is made easier if, instead of diagonalization of H_0 in Hilbert space, the full exact Hamiltonian is considered and diagonalized in limited Hilbert space, because then the task is to find a convenient basis set for the resonance states using the full Hamiltonian. That this is possible can be seen from the Feshbach formalism [2] as used by O'Malley and Geltman [3], according to which

$$H_0 = QHQ + PHP; \quad H' = QHP + PHQ$$

and the eigenstates of QHQ are equivalent to bound eigenstates of H_0 . It can be shown that diagonalization of QHQ in Hilbert space is equivalent to diagonalization of H in Q subspace.

After the Q subspace has been found, the approximation methods appropriate for bound states will apply, on condition that they are restricted only to this subspace. A variational approximation using ψ_{tr} in Q subspace will give the upper bound to the exact eigenvalue of QHQ . ψ_{tr} can be improved by adding terms which also belong to the Q subspace. The truncation method [4] is actually analogous to the Hylleraas-Undheim procedure except that here all configurations are in Q space. The HF approximation using $\psi_{\text{HF}} \in Q$ will give the HF solution QHQ and the correlation energy. In the perturbation-variation method, the Hylleraas condition will give the upper bound to E_2^{exact} of QHQ if $\psi_{\text{tr}} \in Q$ is used, and so on. The requirement for all this, then, is to find the appropriate Q subspace, i.e. a subspace such that $H' = QHP + PHQ$ gives a good width and H_0 – a good energy.

Proper (exact) Q subspaces have been obtained [3] for two-electron compound atoms. For more complex systems, only approximate Q subspaces have been found [5]. For the H^- and He atoms a projection operator was used, which excluded from ψ_{tr} all configurations including $1s$ hydrogenic orbitals. The variation method was used to obtain upper bounds. Good results were obtained, showing that the Q subspace used, was appropriate for two-electron atoms. Working in the same subspace, Chan and Stewart [6] used the perturbation-variation method (applying the Hylleraas condition which, in this case, gives the upper bound for E_2^{exact} of QHQ), to get E_0 , E_1 and E_2 . Inclusion of higher energy terms would give the same results as those of Geltman and O'Malley. Lipsky and Russek used a different Q subspace, ψ_{tr} consisting of configurations excluding the continuum.

For three-electron compound atoms such as He^- , Q subspaces can be used approximating those employed by Geltman and O'Malley for the two-electron case. The Q space is composed of all configurations which do not include the best possible approximate ground state wave functions. The remaining basis is not quite of the same type as the Geltman-O-Malley Q subspace because in this subspace the exact target states were projected out and not the approximate ones.

Hartree-Fock Calculations

In the HF Method, the appropriate integro-differential equations are obtained after optimization of E (see above). The HF equations depend on the requirements of the trial ψ^{HF} . Introduction of the orthogonality requirement in the HF equations would give "constrained HF equations" (abbreviated to CHF). Overlooking this requirement, "unconstrained HF equations" (UHF) are obtained. Usually it is not feasible to solve CHF equations for resonance states, although for two-electron atomic systems it might be possible to apply the Q projection operator to ψ^{HF} to get the corresponding CHF and solve them thus getting the HF energy of QHQ .

The $1/Z$ Perturbation HF Method

This method solves the UHF for resonance states, using the inverse nuclear charge as the perturbation parameter. Only zero and first order equations are solved exactly and the HF energy is obtained to the third order:

$$E^{\text{HF}} = Z^2 E_0^{\text{HF}} + Z E_1^{\text{HF}} + \frac{1}{Z} E_3^{\text{HF}}.$$

Although UHF are being solved, this perturbation method introduces some of the required constraints on $\psi_{\text{res}}^{\text{HF}}$. The zero order UHF are identical to the exact zero order Schrödinger equation for the lower states when the interelectronic interactions are taken as the perturbations. This means that ψ_0^{HF} which is equivalent to ψ_0^{exact} is orthogonal to all lower states (i.e. in the zero order approximation ψ^{HF} in this method is orthogonal to all lower states). A choice of ψ_0^{HF} which fits the experimental requirements (symmetry, spin-state, etc.) gives E_0^{HF} and E_1^{HF} identical to E_0^{exact} of the resonance state (when $\frac{1}{Z} \sum_{i \neq j} \frac{1}{r_{ij}}$ is taken as the perturbation). Therefore discrepancies from exact values will arise only for E_2^{HF} and E_3^{HF} .

It can be shown [7–9] that the unconstrained ψ_1^{HF} if expanded in terms of the zero-order wave functions contains only singly excited states. The exclusion of doubly excited zero order configurations which belong to the lower states leads to a sagging, Δ_s , of the E_2^{HF} value relative to E_2^{exact} . The exclusion of doubly excited configurations of the higher states leads to a raising effect, Δ_r .

Thus, clearly, in UHF solutions E_2^{HF} is not a rigorous upper bound of E_2^{exact} and the discrepancy between E_2^{HF} and E_2^{exact} will depend on Δ_s and Δ_r of a given state. It is reasonable to assume that the method will give good results at least to a second-order if the two effects (Δ_r and Δ_s) are of the same magnitude. The way in which E_3^{HF} differs from E_3^{exact} is unknown.

(If the CHF method is used, fulfilling the proper orthogonality requirements of ψ_1^{HF} with the lower states, E_2^{HF} will be a rigorous upper bound of E_2^{exact} and $E_2^{\text{HF}} > E_2^{\text{exact}}$ will always be obtained because there will be only a raising effect (Δ_r). The same is true for E_2^{HF} of ground states and singly excited states so that in this case E_2^{HF} and E_3^{HF} can be assumed to be the true second and third order HF energies.)

With a proper choice of ψ_0 , the present method gives the exact E_0 and E_1 of the resonance state, and the total energy obtained by including the higher terms, i.e. E_2^{HF} and E_3^{HF} , will approximate closely the experimental value if these last are near E_2^{exact} and E_3^{exact} . However, the deviations of E_2^{UHF} and E_3^{UHF} from the exact values have been shown above to be somewhat uncertain. Therefore their inclusion would not necessarily improve the total energy. For light atoms in particular, E_0 and E_1 are not sufficient, and the higher energy terms are necessary for obtaining good total energies. The calculations done so far on atomic resonance states (He, H^-) show that $(Z^2 E_0 + Z E_1)$ is higher than E_{res} and that $E_2^{\text{UHF}}, E_3^{\text{UHF}}$ have negative values, improving the results. However, it must be remembered that in the present method energy terms higher than E_3 are neglected. This truncation error depends on the convergence of the energy terms. For heavier atoms (larger Z), it would be justified to assume that the truncation error is small, so that the proximity of the calculated resonance energy to the true energy will depend mostly on the proximity of E_2^{HF} and E_3^{HF} to the exact energies. From previous analyses [8] it might be assumed that the deviations of E_2^{HF} (from E_2^{exact}) are small. Unfortunately, this assumption cannot be tested because of lack of sufficient experimental data for heavier atoms (see conclusions).

To summarize, the deviation of E^{HF} (as calculated by the present method) from the true value is due to two factors:

1) The deviation of E_2^{HF} and E_3^{HF} from E_2^{exact} and E_3^{exact} respectively because of – (a) the use of the HF approximation (general to all atomic states) and (b) the use of UHF (specific to excited and resonance states).

2) The truncation of higher energy terms.

Since (a) and (b) in 1) work in opposite directions on E_2^{HF} it may be assumed that E_2^{HF} falls near E_2^{exact} and for E_3^{HF} we may intuitively assume the same.

If factors 1) and 2) are of the same direction, then better results would be obtained for higher atoms.

In order to check the above assumptions, experimental results for the appropriate states of atoms heavier than hydrogen and helium are needed.

Finally, it should be stressed that in order to obtain accurate results corresponding to the real electronic state, ψ^{HF} must be taken as eigenstate of S^2 and L^2 and must include other zero order degenerate states as well. As we shall see, not all these requirements are easily fulfilled for every resonance state and in some cases less accurate results are obtained. One must be aware of these inaccuracies and at least estimate the deviation from the values which would be obtained if the required “true” ψ^{HF} were taken.

Calculations and Results

In the present work, the method described above has been applied to several bound or quasibound excited states of three-electron atomic systems. The states chosen were $1s\ 2s^2\ ^2S$, $1s\ 2s\ 2p\ ^2P$, $2s^2\ 2p\ ^2P$, $1s^2\ 2s(2p)\ ^2S(^2P)$ and the metastable $1s\ 2s\ 2p\ ^4P$ state. The results obtained apply, of course, to the entire Li isoelectronic series (with an appropriate $1/Z$ scaling factor). However, only in the cases of He^- and Li are there data (either theoretical or experimental) with which to

compare the present calculations. Two-electron resonance states [9–14a] were also recalculated and some calculations of bound excited states were made for comparison.

To begin with, single-determinant approximations were made. In order to find the three-electron ψ_1^{HF} and E_2^{HF} , data from two-electron-state calculations were used. To calculate E_3^{HF} , the Runge-Kutta method was used [12].

The results of calculations for He, He⁻ and Li are shown in Table 1, while those for bound three-electron states are given in Table 2. The corresponding experimental values are also given insofar as available. The expressions obtained for the energies are given in Appendix 1.

Discussion

As is seen in Table 1, the deviations from experiment vary considerably. This is due to the differences in the factors influencing the approximations involved in the various resonance states. Therefore, these states will be discussed separately, but there is a general problem which should be discussed first and that is the question of the reference state. Resonance energies are usually given relative to the ground state of the initial system, i.e. for He and He⁻ resonances the reference state is the helium ground state. However, the question remains which value for

Table 1. Comparison of calculated and experimental energies of He, He⁻ and Li states

State	Experimental (eV)	HF (1/Z) (a.u.)	HF (1/Z) ^a (eV)	HF (1/Z) ^b (eV)	Other calculations (eV)
He (e ⁻ He ⁺)					
2s ² 1S	57.82 [15]	-0.71955 -0.77285 ^c	59.41 57.98	58.28 56.82	57.80–57.94 [3, 4, 16–18]
2p ² 1S	62.15 [15]	-0.56226 -0.57427 ^c	62.05 63.37	60.90 62.22	62.06–62.81 [3, 4, 16–18]
2p ² 1D	60.00 [19, 20]	-0.66869	60.79	59.66	60.11 [21]
2s 2p 1D	60.14 [22]	-0.65356	61.20	60.07	59.59–60.27 [3, 4, 6, 11, 16, 17]
2s 2p 3P	58.34 [15]	-0.75444	58.46	57.29	58.20–58.38 [3, 4, 6, 11, 16, 17]
2p ² 3P		-0.70136	59.91	58.78	
He ⁻ (e ⁻ He)					
1s ² 2s 2S	19.30 [23, 28]	-2.14896	20.52	19.37	17.8–19.7 [28–32]
1s 2s 2p 2P	19.5 [9, 26]	-2.14145	20.70	19.55	19.2–19.6 [32–34]
1s ² 2s 2S	0.45–1.1 [35, 40, 41]	-2.83490	1.85	0.71	0.43–4.2 [32, 42]
1s ² 2p 2P		-2.83610	1.82	0.68	
2s ² 2p 2P	57.1 [26, 38, 39]	-0.75176	58.53	57.37	57.3 [32]
1s 2s 2p 4P		-2.17083	19.92		19.79 [36]
Li (e ⁻ Li ⁺)					
1s 2s 2p 4P	57.3 [37]	-5.36516	57.47		57.47 [36]

^a Relative to experimental ground state.

^b Relative to HF ground state.

^c Zero order degeneracy taken into account.

the ground state should be used in the present case: the experimental or the HF result. There are arguments for and against both choices and, as there seems to be no unequivocal answer, both sets are given in Table 1.

Two Electron States

For the $2s^2$ and $2p^2\ ^1S$ states, the calculated value using one determinant would be expected to deviate from experiment more than the other singlet states ($2s\ 2p\ ^1P$ and $2p^2\ ^1D$). The reason for this, of course, is that the use of one determinant for ψ^{HF} including, e.g., a $2s$ one electron function is not enough to describe the experimental $\ ^1S$ resonance state, the actual wave function being a superposition of $2s^2$ and $2p^2$ configuration. This will cause splitting, with two independent linear combinations being obtained. The exact energy calculated from a wave function corresponding to the configuration $2s^2$ in the zero-order approximation will fall between the two linear combinations, i.e. the order will be $a_1(2s^2) + b_1(2p^2)$; $2s^2$; $a_2(2s^2) + b_2(2p^2)$. Thus, in the case of an exact perturbation solution it would be certain that the inclusion of the $2p^2$ configuration would give a lower energy for the $\ ^1S$ state. However in the present method there is some uncertainty in this respect mostly because the truncation errors may differ considerably for each case. It was suggested [3] that inclusion of $(2p^2)$ would lower E^{HF} by 0.011727 a.u. (0.319 eV). The use of extended HF equations [14a] takes into account the zero order degeneracy of $2s^2\ ^1S$ and $2p^2\ ^1S$ and the results are given in Table 1 (see also Appendix 1). They do not quite bear out the predictions. If the experimental ground state is used, the energy obtained for $2s^2\ ^1S$ is very near the experimental value but $2p^2\ ^1S$ deviates from experiment considerably more than in the single-determinant calculation. If the HF ground state is referred to, the situation reverses itself, i.e. good agreement is obtained for $2p^2$ but agreement for $2s^2$ is poorer than in the single-determinant case. Therefore, inclusion of zero order degeneracy does not quite resolve the situation.

In the case of $2s\ 2p\ ^1P$ and $\ ^3P$ as well as $2p^2\ ^1D$, a ψ^{HF} is used which is an eigenstate of S^2 and L^2 and there are no degeneracy effects involved. Therefore, the deviations are due only to factors (1) and (2) detailed above.

Three Electron States

For the $1s\ 2s^2\ ^2S$ state, the unrestricted method was used [13, 13a]. For ground states, the method can be considered a definite improvement of E_2^{HF} , but for resonance states, as mentioned above, this is not necessarily the case (although, in most cases, somewhat better results are probably obtained) and in principle it is not as important to use unrestricted HF for resonances as it is for ground states. The motive conducive to the use of unrestricted HF is the comparative ease in calculation. As single-determinant calculations were made, the ψ^{HF} used was not an eigenstate of S^2 . This inaccuracy affects only the second and third order energies and was presumed small. In order to check this, the restricted E_2^{HF} of this state was calculated and the value obtained was only very slightly higher than the unrestricted value.

The $1s^2 2s^2 S$ or $1s^2 2p^2 P$ so-called single particle resonance is rather different from all other states. The resonance is believed to lie closely above the target state of the compound atom, i.e., $1s^2 {}^1S$ and its existence has been, and still is, the state of the compound atom, i.e., $1s^2 {}^1S$ and its existence has been, and still is, the subject of considerable controversy. If one accepts the explanation that it is caused by the trapping of the electron in the angular momentum barrier of a well set up by the induction effect of the incoming electron on the target, then no S wave single particle resonance would be expected [45]. On the other hand, stabilization technique calculations have resulted in a stable root of S symmetry at approximately the experimental single particle resonance energy [32]. In the present calculations both the S and P states were examined. There is no sagging effect in this case and E_2^{HF} will be higher than E_2^{exact} because ψ_1^{HF} includes only singly-excited zero-order configurations (i.e. E_2^{HF} can be considered the true second-order HF energy). As the values obtained are very close together (Table 1) no conclusions can be drawn from the present calculations as to whether the resonance is of S or P type.

The $1s 2s 2p^4 P$ state is metastable but not autoionizing although adjacent to the continuum, as it does not interact with the continuum states. This means that the HF energy calculations for this state are analogous to those for bound states, E_2^{HF} is an upper bound, and E_3^{HF} is the "true" third order HF energy. For this state, one configuration can be used (α, α, α) because it is an eigenstate of S^2 . Since all three electrons are parallel, the correlation energy should be small and so in this case the deviation from experiment must be attributed mostly to truncation errors.

The value for the $1s 2s 2p^2 P$ state in Table 1 is the result of a single-determinant calculation, with configuration $1s\beta, 2s\alpha, 2p\alpha$. This means that the calculated HF energy is that of a state which is a superposition of the doublet and quartet states, which may be considerably split (in this case the two different spin states begin to separate in the first order energy). An attempt was made to estimate the inaccuracy due to single-determinant use from calculations made on this configuration and the quartet state.

In a three-electron atom or ion where each electron occupies different orbitals, we can represent the HF wave function by 8 different determinants which are degenerate in the zero-order approximations: (α, α, α) , (β, β, β) , (α, β, α) , (β, α, α) , (α, α, β) , (α, β, β) , (β, α, β) and (β, β, α) .

In order to obtain an HF wave function which is an eigenstate of S^2 , the spin projection operator technique can be used so as to get 8 independent linear combinations which give wave functions which are eigenstates of S^2 .

The results are given in Table 3. $\psi_a, \psi_b, \psi_c,$ and ψ_d belong to the quartet state, $\psi_e, \psi_f, \psi_g,$ and ψ_h belong to the doublet (see Table 2). The quartet and doublet states are degenerate in the zero order, but in higher order approximations the states separate. (There is splitting between the (ψ_e, ψ_f) and (ψ_g, ψ_h) states also.) In the present calculations, as described above, only one determinant was used. For the quartet state the (α, α, α) configuration was used, which gives the true value for this state. For the doublet state, separate calculations were carried out for the E^{HF} of each of the determinants (α, β, α) , (α, α, β) , (β, α, α) . Each determinant gave a different energy because none describes a pure doublet state, but rather a

Table 2. Comparison of Hartree-Fock and experimental energies for some bound excited three-electrons states

Z	$E_{1s^2 2s}^{\text{exp}}$ (a.u.) [43]	$E_{1s^2 2p}^{\text{exp}}$ (a.u.) [43]	$E_{1s^2 2s}^{\text{HF}}$ (a.u.) [44]	$E_{1s^2 2s}^{\text{HF}, 1/Z}$ (a.u.)	$E_{1s^2 2p}^{\text{HF}, 1/Z}$ (a.u.)	ΔE^{exp} (eV)	$\Delta E^{\text{HF}, 1/Z}$ (eV)	$\Delta E_{\text{exp}}^{\text{HF}^a}$ (eV)
3	-7.4787	-7.4107	-7.4327	-7.4285	-7.3498	1.847	2.143	3.507
4	-14.3267	-14.1812	-14.2774	-14.2764	-14.1223	3.959	4.194	5.561
5	-23.4298	-23.2094	-23.3760	-23.3761	-23.1271	5.998	6.773	8.237
6	-34.7873	-34.4931	-34.7261	-34.7265	-34.4264	8.004	8.167	9.819
7	-48.4000	-48.0326	-48.3269	-48.3275	-47.9553	9.998	10.127	12.099
8	-64.2698	-63.8290	-64.1780	-64.1787	-63.7349	11.993	12.077	14.554

$$^a \Delta E_{\text{exp}}^{\text{HF}} = E_{1s^2 2p}^{\text{HF}, 1/Z} - E_{1s^2 2s}^{\text{exp}}.$$

Table 3. HF S^2 eigenstate wave functions

	S^2	$S_{1z} + S_{2z} + S_{3z}$
$\psi_a = (\alpha, \alpha, \alpha)$	$\frac{15}{4} \hbar^2$	$\frac{3}{2} \hbar$
$\psi_b = \frac{1}{\sqrt{3}} [(\alpha, \alpha, \beta) + (\alpha, \beta, \alpha) + (\beta, \alpha, \alpha)]$	$\frac{15}{4} \hbar^2$	$\frac{1}{2} \hbar$
$\psi_c = \frac{1}{\sqrt{3}} [(\beta, \alpha, \beta) + (\beta, \beta, \alpha) + (\alpha, \beta, \beta)]$	$\frac{15}{4} \hbar^2$	$-\frac{1}{2} \hbar$
$\psi_d = (\beta, \beta, \beta)$	$\frac{15}{4} \hbar^2$	$-\frac{3}{2} \hbar$
$\psi_e = \frac{1}{\sqrt{6}} [2(\beta, \alpha, \alpha) - (\alpha, \alpha, \beta) - (\alpha, \beta, \alpha)]$	$\frac{3}{4} \hbar^2$	$\frac{1}{2} \hbar$
$\psi_f = \frac{1}{\sqrt{6}} [2(\beta, \alpha, \beta) + (\beta, \beta, \alpha) - 2(\alpha, \beta, \beta)]$	$\frac{3}{4} \hbar^2$	$-\frac{1}{2} \hbar$
$\psi_g = \frac{1}{\sqrt{2}} [(\alpha, \alpha, \beta) - (\alpha, \beta, \alpha)]$	$\frac{3}{4} \hbar^2$	$\frac{1}{2} \hbar$
$\psi_h = \frac{1}{\sqrt{2}} [(\beta, \alpha, \beta) - (\beta, \beta, \alpha)]$	$\frac{3}{4} \hbar^2$	$-\frac{1}{2} \hbar$

superposition of a quartet and doublet and so the (exact) energy calculated from one configuration must fall between the quartet and doublet states. However, the differences were small.

Whether the E^{HF} calculated using one configuration differs considerably from the E^{HF} which would be obtained if one of the doublet states is used, can be estimated using the results of the quartet states and the results of the (β, α, α) configuration (referred to as ψ thereafter). This configuration is a linear combination $\psi = \sqrt{\frac{2}{3}} \psi_e + \frac{1}{\sqrt{3}} \psi_b$. Since $\langle \psi_e | \psi_b \rangle = 0$ and $\langle \psi_e | H | \psi_b \rangle = 0$. It can be shown that $E_1^{\text{exact}} = \frac{2}{3} E_{1d}^{\text{exact}} + \frac{1}{3} E_{1q}^{\text{exact}}$ and similarly for E_2 and E_3 , where d, q are the doublet and quartet states.

E_{1d} of the ψ_e configuration was calculated exactly because only the zero order wave-function was used. The result obtained was $E_{1d} = 0.6049965$ a.u.

as compared to 0.5854873 a.u. previously. Thus, for He^- we obtain

$$\Delta E_1 = 2(E_1 - E_{1d}) = 0.039984 \text{ a.u.} \sim 1.1 \text{ eV}.$$

For E_2^{HF} only an estimate can be made because the 1 : 2 splitting is not exact in this case. However, if we assume that E_2^{HF} does not fall far from the exact value of E_2 (and in the same direction), this splitting can be used for a rough estimate. The result is $E_{2d}^{\text{HF}} \sim 0.36 \text{ a.u.}$ so that $\Delta E_2^{\text{HF}} = (E_2^{\text{HF}} - E_{2d}^{\text{HF}}) \sim -0.04 \text{ a.u.} = -1.1 \text{ eV}$. This means that the true doublet configuration would raise E_1 by 1.1 eV and lower E_2 by about the same amount.

For E_3^{HF} the separation is small so that the inaccuracy of using only the (β, α, α) determinant is probably negligible in this case.

For $Z > 2$, ZE_1 is raised more than E_2 is lowered, and so the E^{HF} this determinant gives is lower than what the doublet configuration would give. In such a case it is probably more accurate to use the E_1 calculated from the doublet configuration.

Conclusions

The above results on He and He^- resonances show that this method can be applied as a convenient and rapid technique for obtaining approximate values of energies for (doubly excited) resonance states.

A clear advantage is, of course, that once the HF equations are solved for a specific electronic state, all the E^{HF} energies for all nuclear charges can be derived. However, awareness of the possible deviations should be stressed. As mentioned above, these are dependent on Z . A larger Z value reduces the truncation error so that the deviation is due mainly to $E_2^{\text{HF}} - E_2^{\text{exact}}$. If E_2^{HF} , because of the "raising" and "sagging" effects, is not far from E_2^{exact} , the deviation of E^{HF} for higher Z becomes smaller than that found for $Z=2$. To study this point, it would be interesting to investigate energies of doubly excited states (for 2 and 3 electrons) for $Z > 2$ (i.e. Li, Be^+), using more elaborate approximation methods. Alternatively, or even preferably, further experimental work (for higher Z) would be most useful. As the experimental results now available for comparison are confined almost entirely to He and He^- , where $Z=2$, we do not, as yet, know whether for higher Z better results are indeed obtained or whether the deviations are of the same order of magnitude. For the single Li state available for comparison, the above prediction is borne out as seen in Table 1.

A comparison with the bound states given in Table 2 is also interesting in this respect. It is clear from Table 2 that in these cases the agreement of the HF. $1/Z$ method with Roothaan's results is better for higher Z so that truncation errors decrease for higher Z . As to the correlation energy, its effect also is smaller (percentagewise) for higher Z ($\Delta E_{\text{exp}}^{\text{HF}}$ in Table 2). If the difference between the HF ground and excited states is examined, it is seen that agreement is much better than for the $\Delta E_{\text{exp}}^{\text{HF}}$ case. This means that the correlation energy is similar for both states. Here agreement with experiment is excellent for higher Z showing the effect of truncation errors to be practically nonexistent. It should be mentioned in this context that although the *method* is certainly more accurate for these states than for resonances, the *results* obtained are sometimes better for resonances,

as a comparison of the two Tables shows. This is, of course, partly fortuitous, but is partly due to the sagging effect appearing for resonances but not for bound states.

The use of this method for atoms containing more than three electrons is still simple (if we use single-determinant approximations). Therefore, the method may be used to get approximate values for more complex atomic systems. A comparison of the results we get for two-electron and three-electron resonances shows that, contrary to expectations, the results for three-electron systems are much more homogeneous and better related to the experimental values. This is surprising because the convergence of energy becomes presumably slower with increase in number of electrons. The differences in truncation errors would therefore seem to be small and one would expect to get deviations of not more than 1–2 eV for larger systems.

Appendix 1

Hartree-Fock Energy Expressions

Two Electrons

$$E^{\text{HF}}(2p^2\ ^1S) = -\frac{1}{4}Z^2 + 0.2167968Z - 0.0556355 - \frac{0.0010515}{Z}$$

$$E^{\text{HF}}(2p^2\ ^1D) = -\frac{1}{4}Z^2 + \frac{237Z}{1280} - 0.038725 - \frac{0.000557}{Z}$$

$$E^{\text{HF}}(2s^2\ ^1S) = -\frac{1}{4}Z^2 + \frac{77}{512}Z - 0.0200065 - \frac{0.0006465}{Z}$$

$$E^{\text{HF}}(2s\ 2p\ ^1P) = -\frac{1}{4}Z^2 + \frac{49}{256}Z - 0.342419 - \frac{0.0043096}{Z}$$

$$E^{\text{HF}}(2s\ 2p\ ^3P) = -\frac{1}{4}Z^2 + \frac{17}{128}Z - 0.0194185 - \frac{0.0012992}{Z}$$

$$E^{\text{EHF}}(2s^2\ ^1S) = -\frac{1}{4}Z^2 + 0.122952443Z - 0.026327412 + \frac{0.0151507}{Z} + 0(Y_{Z^2})$$

$$E^{\text{EHF}}(2p^2\ ^1S) = -\frac{1}{4}Z^2 + 0.244235059Z - 0.057314532 - \frac{0.0108466}{Z} + 0(Y_{Z^2})$$

$$E^{\text{HF}}(2p^2\ ^3P) = -\frac{1}{4}Z^2 + \frac{21}{128}Z - 0.029338 - \frac{0.000282}{Z}$$

Three Electrons

$$E^{\text{HF}}(1s\ 2s^2\ ^2S) = \left(-\frac{3}{4}\right)Z^2 + 0.5481958Z - 0.2249077 - \frac{0.040878}{Z}$$

$$^1 E^{\text{HF}}(1s\ 2s\ 2p\ ^2P) = \left(-\frac{3}{4}\right)Z^2 + 0.5854873Z - 0.3195984 - \frac{0.0135531}{Z}$$

¹ This expression belongs to the $(1s\beta, 2s\alpha, 2p\alpha)$ configuration. The calculations for $(1s\alpha, 2s\beta, 2p\alpha)$ and $(1s\alpha, 2s\alpha, 2p\beta)$ give

$$E^{\text{HF}}(\alpha, \beta, \alpha) = \left(-\frac{3}{4}\right)Z^2 + 0.5977136Z - 0.2767546 - \frac{0.0622646}{Z},$$

$$E^{\text{HF}}(\alpha, \alpha, \beta) = \left(-\frac{3}{4}\right)Z^2 + 0.5928363Z - 0.2834884 - \frac{0.0756959}{Z}.$$

$$\begin{aligned}
 E^{\text{HF}}(1s^2 2s^2 S) &= \left(-\frac{9}{8}\right)Z^2 + 1.02280Z - 0.354811 - \frac{0.05134}{Z} \\
 E^{\text{HF}}(1s 2s 2p^4 P) &= \left(-\frac{3}{4}\right)Z^2 + 0.546469Z - 0.2361691 - \frac{0.0552021}{Z} \\
 E^{\text{HF}}(2s^2 2p^2 P) &= \left(-\frac{3}{8}\right)Z^2 + 0.445311Z - 0.1439054 - \frac{0.0298466}{Z} \\
 E^{\text{HF}}(1s^2 2p^2 P) &= \left(-\frac{9}{8}\right)Z^2 + 1.09352Z - 0.469779 - \frac{0.106677}{Z}
 \end{aligned}$$

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