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Hartree–Fock Calculations for Excited Rydberg States

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A method is introduced which allows to compute self-consistent restricted Hartree–Fock wave functions for excited Rydberg configurations. The concepts of reorganization and electron correlation of Rydberg states are discussed. As an illustration Hartree–Fock calculations for the (1s)(nl) Rydberg series of He are presented.

Key words: Excited states – Correlation – Reorganization – He-atom.

1. Introduction

The concepts of electron correlation and reorganization are so familiar, that they need not be introduced. Both these concepts are characterized by the fact that they are based on mathematical rather than on physical ideas, since neither can be measured experimentally. Nevertheless electron correlation and reorganization facilitate the physical interpretation of electronic wave functions because the complicated energy of a correlated wave function can (at least approximately) be partitioned into contributions which arise from physically distinguishable effects. A classical example is Meyer's study on the ionization of H_2O [1]. The ionization energies are analyzed in terms of Koopmans' energies, loss of correlation energy caused by the abstraction of an electron, reorganization of the orbitals and so on. In this case the Hartree–Fock single determinant wave function of the neutral molecule serves as a reference function with respect to which reorganization and correlation energies can be calculated.

Although the concepts of reorganization and correlation have proved useful for understanding the ground and low lying electronic states, they are in general not applied in the discussion of higher excited states. There are two reasons for this: First a reference function has to be calculated which can serve as a starting point for the reorganization of the orbitals. It may be difficult to define a physically

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significant reference function. Second the distinction of reorganization and correlation implies that the orbitals of the reference function can be relaxed selfconsistently, i.e. that a restricted Hartree–Fock function for the excited state can be calculated. The techniques for such calculations are by no means standardized.

In the following two sections it will be shown how the concepts of reorganization and correlation can be applied to Rydberg states.

2. The Frozen Core Aprroximation for Rydberg States

An electronic state is called a Rydberg state, if a single electron is moving in an expanded orbital and is attracted by a relatively small ionic core. The shape of the Rydberg orbital is determined mainly by the interaction with the charge of the core and by orthogonality constraints with respect to the (occupied) core orbitals and, perhaps, to lower (unoccupied) Rydberg orbitals. The prototype for Rydberg orbitals are the electronic states of the hydrogen atom where the core reduces to a proton.

Approximate single-configuration wave functions for Rydberg states can be obtained with the frozen core (FRC) method. This method can be traced back to Mulliken [2] and has been introduced into quantum chemistry by Lefebvre-Brion and Moser [3], and by Hunt and Goddard [4] as the method of improved virtual orbitals. In connection with excited Rydberg states however we prefer to term it FRC [5].

First a restricted Hartree–Fock (RHF) calculation for the bare core is carried out. This wave function may represent a closed-shell or an open-shell configuration, a ground or an excited state. Then the subspace of the occupied core orbitals is projected out of the orbital basis, and with the remaining orbitals the single particle problem for the Rydberg electron is solved. This method has repeatedly been applied to the calculation of atomic and molecular Rydberg orbitals [6–8]. To be precise the Rydberg orbitals are eigenfunctions of the operator

$$\sum_{v} |\phi_v)(\boldsymbol{h} + 2\boldsymbol{J}^d - \boldsymbol{K}^d + \boldsymbol{J}^s \pm \boldsymbol{K}^s)(\phi_v| \tag{1}$$

where the superscripts denote doubly and singly occupied core orbitals and the sum extends over the virtual orbitals ϕ_v. Eq. (1) applies for a doublet Rydberg state with closed-shell core if the potentials J^s and K^s are omitted, and for singlet or triplet Rydberg states if the plus or minus sign is used, respectively. It can be understood as a Brillouin condition optimizing a singly occupied Rydberg orbital ϕ_R with respect to the space of the unoccupied orbitals. The eigenvalues, ε_R, of Eq. (1) are called orbital energies. If ε_k is added to the energy expectation value of the bare core we get the total electronic energy of the kth Rydberg state in the FRC approximation. Hence, the ε_R can serve as approximate ionization energies of the Rydberg states [2].

According to the Hylleraas-Undheim theorem [9, 10] the energy of the kth Rydberg state of a given symmetry in the FRC approximation is an upper bound for the exact kth energy eigenvalue. This theorem can be invoked here because the FRC wave functions can also be interpreted as the eigenfunctions of a limited CI-treatment for all single excitations of the Rydberg electron in the field of a fixed core. The consequences of this fact shall be discussed in Sect. 4.

We will use the FRC single configuration wave functions as reference functions for the Rydberg states. The reorganization energy of the kth Rydberg state can be defined as the energy difference between the kth FRC and the kth excited state RHF solution where the corresponding reorganized core orbitals are occupied. The difference between the RHF energy and the exact non-relativistic energy is defined as the correlation energy [11].

3. Hartree–Fock-Theory for Excited Rydberg States

In the past, several methods have been invented for the calculation of self-consistent single-configuration wave functions of electronically excited states. These methods have been applied to inner shell ionizations [12] and valence excited Koopmans' configurations [13] and also to lower excited states [14–17]. Froese has developed a formalism which was applied to the calculation of atomic Rydberg states [18, 19]. All these methods yield orbitally optimized wave functions for different electronic states of a system which are mutually non-orthogonal [20, 21]. In exceptional cases even the set of occupied orbitals of an individual excited configuration has been chosen non-orthogonal [22]. The method which we present below does not differ in this respect from earlier attempts, but has the advantage that it has been specifically designed for the calculation of Rydberg states and leads to a perspicuous formalism which can be easily programmed.

This method is based on the familiar formalism for the treatment of open-shell configurations in the RHF approximation (e.g. [23, 24]). A Brillouin condition has to be formulated [25–27] for any pair of orbital subspaces whose mixing may lead to an improved energy of the wave function. Each Brillouin condition yields an effective operator and these operators have to be combined into a single Fock matrix by means of the projection operator technique. The Fock matrix is diagonal if it is written in the basis of the self-consistent orbitals.

If this formalism is applied to the calculation of excited Rydberg configurations one is confronted with the necessity of preventing the excited Rydberg orbital from collapsing and transforming to a lower orbital. This can be achieved with an iterative procedure where a number of RHF iterations for the core orbitals are performed and then an FRC calculation for the Rydberg orbital is carried out and the process is repeated, until selfconsistency is reached. In the course of the RHF steps all the off-diagonal elements of the Fock matrix connecting the occupied Rydberg orbital with unoccupied orbitals are put equal to zero in order to avoid any mixing of occupied and unoccupied Rydberg orbitals. The FRC step on the other hand is equivalent to an elimination of all the matrix elements influencing the core orbitals, as is shown in Fig. 1.

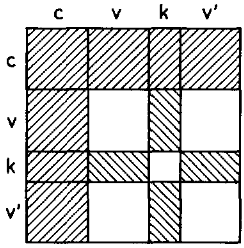

Fig. 1. Fock matrix for excited Rydberg configurations

/// matrix elements omitted for the FRC step.
\\\ elements zeroed during the reorganization of the core orbitals.
The entries of the matrix have the following meaning:
c core orbitals (occupied),
k occupied Rydberg orbital,
v, *v'* unoccupied orbitals

The FRC step yields a manifold of Rydberg orbitals which have been calculated in the field of the reorganized core. The procedure leads to a stable solution if, after each FRC calculation, the *k*th Rydberg orbital is selected to be occupied for the next RHF iterations of the core. Selfconsistency is achieved as soon as the orbitals will not be modified anymore by either step. In this situation all the off-diagonal elements of the Fock matrix whcih were zeroed in the course of the iteration will vanish automatically. Therefore no artificial condition is imposed on the self-consistent wave function other than requiring its energy to be an upper bound of the *k*th exact solution of the Schrödinger equation.

4. Discussion of Special Cases

We are used to the situation that the energy of a wave function is lowered if reorganization and electron correlation corrections are included. In this case the signs of ΔE(reorg.) and ΔE(corr.) are defined to be negative. For excited states, however, both energy contributions can be positive as well. More often positive contributions to the total (negative) correlation energy lead to unusual correlation corrections for excitation on binding energies similar to those reported by Bagus [12] for the case of core ionization. Positive correlation effects appear when in the exact wave function the Hartree–Fock configuration is mixed with a lower configuration such that the energy is raised. Physically this can be interpreted in analogy to the (negative) correlation energy of a ground state wave function: In the RHF approximation the electron repulsion is underestimated with respect to a correlated function, where the electrons are forced to be closer to each other than a single configuration picture would predict. As a rule Rydberg states exhibit effects of positive correlation – or "anticorrelation", when there is a different configuration of the same symmetry at lower energies. An example is provided by the $(1s)^2(2s)(nd):{}^1D_g$-Rydberg series of Be which is shifted to higher energies by interaction with the $(1s)^2(2p)^2:{}^1D_g$ configuration. In this case the Hylleraas–Undheim theorem invoked above says that the $\ldots(2s)(3d):{}^1D_g$ single configuration energy is an upper bound to the exact energy of the lowest ${}^1D_g$ state which turns out to have $\ldots(2p)^2$ configuration [28]. The RHF energy of $\ldots(2s)(4d)$ is an upper bound to the exact energy of $\ldots(2s)(3d)$ and so on. Positive reorganization effects appear when in the FRC approximation the interaction with a lower configuration is neglected, which will be included in the

RHF treatment. As an example we discuss the $(1s)(ns):{}^1S_g$ Rydberg series of He. In the FRC approximation the ns orbitals are optimized assuming a fixed $1s$ orbital of He^+. RHF orbitals are chosen such that the matrix element of the Hamiltonian between $(1s)(ns)$ and any $(1s)(ks)$ or $(ks)(ns)$ singlet configuration ($k \neq 1, n$; orthogonal orbitals assumed) vanishes. This is achieved with an appropriate definition of the $1s-ks$ and $ns-ks$ matrix elements of the Fock matrix. The crucial point is the inclusion of the $(1s)^2$ and $(ns)^2$ configurations. The $1s-ns$ element of the Fock matrix can be used for handling one arbitrarily chosen linear combination of them. We have studied the following possibilities:

(i) Brillouin variant. The $1s-ns$ element of the Fock matrix is defined as the matrix element of the Hamiltonian between $(1s)(ns)$ and the additivie combination $((1s)^2+(ns)^2)/\sqrt{2}$. Hence

$$\boldsymbol{F}_{1s,ns} = 2\boldsymbol{h}_{1s,ns} + \boldsymbol{K}^{(1s)}_{1s,ns} + \boldsymbol{K}^{(ns)}_{1s,ns}$$

where $\boldsymbol{F}, \boldsymbol{h}, \boldsymbol{K}$ denote the Fock, single particle and exchange operators. This choice leads to a self-consistent wave function in the sense of the Brillouin theorem because the CI matrix element to any singly substituted configuration vanishes. Here a configuration is called singly substituted when the CI matrix element contains formally a contribution of the h operator. The CI element with a complementary combination $((1s)^2-(ns)^2)/\sqrt{2}$ consists only of electron interaction contributions.

(ii) Hylleraas variant. The $1s-ns$ element can be used for ensuring that the RHF energy of a Rydberg state is a true upper bound to the corresponding

Table 1. $(1s\,nl)$ Rydberg states of He: Ionization energies

		$-\varepsilon$(exptl.)[a]	$-\varepsilon$(FRC)[b]	$-\varepsilon$(RHF)	$-\Delta E$(reorg.)	$-\Delta E$(corr.)[c]
${}^1S^d$	$2s$	0.145974	0.155255	0.145511	−0.009744	0.000463
	$3s$	0.061272	0.063587	0.061202	−2385	70
	$4s$	0.033587	0.034497	0.033565	−932	22
	$5s$	0.021177	0.021625	0.021167	−458	10
	$6s$	0.014563	0.014816	0.014558	−258	5
	$7s$	0.010626	0.010782	0.010622	−160	4
${}^1S^e$	$2s$			0.123906	−0.031349	0.022068
	$3s$			0.054864	−8723	6408
	$4s$			0.030925	−3572	2662
	$5s$			0.019830	−1795	1347
	$6s$			0.013790	−1026	773
	$7s$			0.010147	−636	479
${}^1S^f$	$2s$			0.169851	0.014596	−0.023877
	$3s$			0.066644	3057	−5372
	$4s$			0.035630	1133	−2043
	$5s$			0.022168	543	−991
	$6s$			0.015118	302	−555
	$7s$			0.010967	185	−341

Table 1 (*cont.*)

		$-\varepsilon$(exptl.)[a]	$-\varepsilon$(FRC)[b]	$-\varepsilon$(RHF)	$-\Delta E$(reorg.)	$-\Delta E$(corr.)[c]
^3S	$2s$	0.175237	0.174242	0.174247	0.000005	0.000990
	$3s$	0.068691	0.068482	0.068482	0	209
	$4s$	0.036513	0.036434	0.036434	0	79
	$5s$	0.022619	0.022580	0.022580	0	39
	$6s$	0.015378	0.015355	0.015355	0	23
	$7s$	0.011130	0.011116	0.011116	0	14
^1P	$2p$	0.123839	0.122445	0.122460	0.000015	0.001379
	$3p$	0.055146	0.054736	0.054737	1	409
	$4p$	0.031069	0.030895	0.030895	0	174
	$5p$	0.019906	0.019815	0.019815	0	91
	$6p$	0.013834	0.013781	0.013781	0	53
	$7p$	0.010169	0.010135	0.010135	0	34
^3P	$2p$	0.133173	0.131316	0.131431	0.000115	0.001742
	$3p$	0.058083	0.057579	0.057587	8	496
	$4p$	0.032325	0.032119	0.032120	1	205
	$5p$	0.020551	0.020446	0.020447	1	104
	$6p$	0.014208	0.014147	0.014147	0	61
	$7p$	0.010405	0.010366	0.010366	0	39
^1D	$3d$	0.055621	0.055543	0.055543	0.000000	0.000078
	$4d$	0.031280	0.031242	0.031242	0	38
	$5d$	0.020016	0.019995	0.019995	0	21
	$6d$	0.013899	0.013885	0.013885	0	14
	$7d$	0.010211	0.010201	0.010201	0	10
^3D	$3d$	0.055636	0.055569	0.055569	0.000000	0.000067
	$4d$	0.031289	0.031257	0.031257	0	32
	$5d$	0.020021	0.020003	0.020003	0	18
	$6d$	0.013902	0.013890	0.013890	0	12
	$7d$	0.010212	0.010204	0.010204	0	8

[a] Binding energies with respect to He^+ (Ref. [28]). 1 a u (^4He)~218844.6 cm^{-1}.

[b] $E(He^+)=1.999996$ a.u. with the basis set used.

[c] ε(RHF)$-\varepsilon$(exptl.); relativistic contributions neglected.

[d] Brillouin variant, see text.

[e] Hylleraas variant, see text.

[f] Hellmann variant, see text.

exact energy. To that purpose it has to be defined as the CI matrix element of the configurations $(1s)(ns)$ and $(1s)^2$. (It is assumed that the energy of $(1s)^2$ is below $(1s)(ns)$, in contrast to $(ns)^2$). Hence

$$\boldsymbol{F}_{1s,ns}=\sqrt{2}(\boldsymbol{h}_{1s,ns}+\boldsymbol{K}^{(1s)}_{1s,ns}).$$

Arguing along the same lines as Guest and Saunders [13] one can see that in this case the RHF energy corresponds to the nth eigenvalue of a limited CI calculation. Since the FRC energy is an upper bound only to the $(n-1)$th state of ^1S_g symmetry positive reorganization effects can be expected (see Table 1).

(iii) Hellmann variant. Neither of these methods optimizes the energy expression of the $(1s)(ns)$ singlet configuration. As a consequence both yield wave function which violate the virial theorem. This theorem will be obeyed by the RHF function if the $1s-ns$ element is defined as the CI matrix element of $(1s)(ns)$ and the subtractive combination $(ns)^2-(1s)^2)/\sqrt{2}$. Hence

$$\boldsymbol{F}_{1s,ns}=\boldsymbol{K}^{(2s)}_{1s,ns}-\boldsymbol{K}^{(1s)}_{1s,ns}.$$

In this case the reorganization energies will be negative for all $(1s)(ns):{}^1S_g$ Rydberg states. Table 1 shows that these are over-compensated by positive correlation energies.

5. Example: Rydberg States of Helium

It is the purpose of this section to demonstrate the feasibility of the method derived above with a numerical example. Further results will be presented in a forthcoming paper.

We have calculated the RHF wave functions for the $(1s)(nl)$ Rydberg states of He with $n\leq 7$ and $l\leq 2$. For the Rydberg orbitals we have used the Gaussian basis specified in Ref. [6]. For core orbitals and penetration effects this set was augmented by a $10s$, $5p$, $2d$ basis with exponents up to 4700 (s), 11 (p) and 0.56 (d). The total basis consists of 50 uncoupled Gaussians. For the $(1s)(ns)^1S_g$ series we have tested all the three variants of the method presented in Sect. 4.

The calculated energies (Table 1) agree with the results of earlier authors [22, 29] except for the ${}^1S_g$ series. The Brillouin variant using orthogonal orbitals within each configuration but violating the Hellman–Feynman theorem yields results slightly closer to the experiment and to the values of the corresponding triplet states than methods employing non-orthogonal orbitals [22]. With the Hellmann and Hylleraas variants we find large reorganization and correlation corrections which nearly cancel out.

In his treatise on atomic spectra Edlen [30] has made extensive use of the concepts of effective quantum numbers and quantum defects. With FRC and RHF calculations for the Rydberg states it is possible to separate the contributions of the reorganization and correlation effects within each series according to

$$n^*(\text{exptl.})=n^*(\text{FRC})+\Delta n^*(\text{reorg.})+\Delta n^*(\text{corr.})$$

(if relativistic effects can be neglected; see Table 2). $n^*(\text{FRC})$ may be divided further into an integer principal quantum number n and a quantum defect $\delta(\text{FRC})$ as calculated in the FRC approximation:

$$n^*(\text{FRC})=n-\delta(\text{FRC}).$$

The observed quantum defects are, as a rule, nearly constant. Our results show that there is practically no reorganization (except for ${}^1S_g$) and an almost constant correlation contribution. (This can also be regarded as a proof for the numerical stability of our calculations). An eventual increase of the observed quantum

Table 2. $(1s\,nl)$ Rydberg states of He: Effective quantum numbers[a]

		n^*(exptl.)	n^*(FRC)	n^*(RHF)	$-\Delta n^*$(reorg.)[b]	$-\Delta n^*$(corr.)[c]
^1S[d]	$2s$	1.851	1.795	1.854	−0.059	0.003
	$3s$	2.857	2.804	2.858	−0.054	0.001
	$4s$	3.858	3.807	3.860	−0.053	0.001
	$5s$	4.859	4.808	4.860	−0.052	0.001
	$6s$	5.859	5.809	5.860	−0.051	0.001
	$7s$	6.860	6.810	6.861	−0.051	0.001
^1S[e]	$2s$			2.009	−0.214	0.158
	$3s$			3.019	−0.215	0.162
	$4s$			4.021	−0.214	0.163
	$5s$			5.021	−0.213	0.162
	$6s$			6.021	−0.212	0.162
	$7s$			7.020	−0.210	0.160
^1S[f]	$2s$			1.716	0.079	−0.135
	$3s$			2.739	0.065	−0.118
	$4s$			3.746	0.061	−0.112
	$5s$			4.749	0.059	−0.110
	$6s$			5.751	0.058	−0.108
	$7s$			6.752	0.058	−0.108
^3S	$2s$	1.689	1.694	1.694	0	0.005
	$3s$	2.698	2.702	2.702	0	0.004
	$4s$	3.701	3.705	3.705	0	0.004
	$5s$	4.702	4.706	4.706	0	0.004
	$6s$	5.702	5.706	5.706	0	0.004
	$7s$	6.703	6.707	6.707	0	0.004
^1P	$2p$	2.009	2.021	2.021	0	0.012
	$3p$	3.011	3.022	3.022	0	0.011
	$4p$	4.012	4.023	4.023	0	0.011
	$5p$	5.012	5.023	5.023	0	0.011
	$6p$	6.012	6.023	6.023	0	0.011
	$7p$	7.012	7.024	7.024	0	0.012
^3P	$2p$	1.938	1.951	1.950	0.001	0.012
	$3p$	2.934	2.947	2.947	0	0.013
	$4p$	3.933	3.946	3.946	0	0.013
	$5p$	4.933	4.945	4.945	0	0.013
	$6p$	5.932	5.945	5.945	0	0.013
	$7p$	6.932	6.945	6.945	0	0.013
^1D	$3d$	2.998	3.000	3.000	0	0.002
	$4d$	3.998	4.001	4.001	0	0.003
	$5d$	4.998	5.001	5.001	0	0.003
	$6d$	5.998	6.001	6.001	0	0.003
	$7d$	6.998	7.001	7.001	0	0.003
^3D	$3d$	2.998	3.000	3.000	0	0.002
	$4d$	3.998	4.000	4.000	0	0.002
	$5d$	4.997	5.000	5.000	0	0.003
	$6d$	5.997	6.000	6.000	0	0.003
	$7d$	6.997	7.000	7.000	0	0.003

[a] $n^*=\sqrt{-1/2\varepsilon}$; ε-values from Table 1.

[b] n^*(RHF)$-n^*$(FRC).

[c] n^*(exptl.)$-n^*$(RHF); relativistic contributions neglected.

[d,e,f] see Table 1.

defect (e.g. through the ^3P series) or a decreasing trend (^1S, ^3S, ^1P) is reproduced by the δ(FRC). Singlet–triplet splittings are nearly exact even in the FRC approximation. A similar behaviour of the decomposition of the effective quantum numbers has also been obtained for the Rydberg series of Li [6]. It had to be expected since it is rather improbable that the almost constant defects, as observed in the spectra, result from physically different effects with non-constant contributions to the quantum defect.

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