

## ON HARTREE-FOCK EXPECTATION VALUES

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### ABSTRACT:

A discussion of the accuracy of the expectation values of one-electron operators using Hartree-Fock versus exact eigenfunctions is given. Some results from the literature for atoms and also calculated values in simple model systems are analysed showing that the over-all trends usually assumed do exist, but that in many cases important exceptions for particular operators arise. Such exceptions are related to some well-defined characteristics of Hartree-Fock functions in turn associated to the analytical behaviour of the potentials involved and to general aspects such as the validity of the Virial Theorem and the co-existence of one- and two-electron terms in the hamiltonian. All these aspects combine to produce important amplifications or reductions in the errors of Hartree-Fock values for certain operators.

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## I. INTRODUCTION

Seldom has an approximation technique received more careful analysis than the Hartree-Fock (H-F) self-consistent scheme. In particular the question of the accuracy of H-F expectation values other than the total energy received early attention<sup>1</sup>. More recently estimations of H-F errors showing general trends for different types of operators<sup>2</sup> (one- or two-electron types) and for operators that weigh different regions of the atom<sup>3</sup> have been obtained. Unfortunately the validity of the proposed general trends for a reasonable number of interesting operators is not possible in most atomic systems because: i) functions accurate enough to be deemed as "exact" wavefunctions (wf) exist only for the very lightest atoms, and ii) experimental results do not exist for the values of many analytically interesting operators, and when they exist it is difficult to assess the relative accuracy of measurements of very different properties. We shall henceforth proceed to show that for those atomic cases where accurate wf do exist and for the completely solvable model system of many-electron atoms developed by Moshinsky and co-workers<sup>4</sup>, such general trends are found but also very important exceptions appear. A thorough discussion of the origin and character of these exceptional cases is given.

## II. HARTREE-FOCK VERSUS EXACT EXPECTATION VALUES

For the discussion of the exactly solvable model of atoms called the pseudo atom the reader is referred to refs. 4-6. Let us just remember that it is a model where attractive and repulsive Coulomb forces are replaced by harmonic oscillator ones. As said above this system has the advantage of being exactly solvable and here approximate expectation values are readily tested. In fact, recent calculations by Moshinsky and Synek<sup>5</sup> showed that the ratio of the moments of the charge distribution:

$$R_k = [\int r^{2k} \rho_{\text{HF}}(r) d\tau] / [\int r^{2k} \rho_{\text{ex}}(r) d\tau] \quad (1)$$

decreases as  $k$  increases. In (1)  $\rho_{\text{HF}}(r)$ ,  $\rho_{\text{ex}}(r)$  are the H-F and exact charge densities. This was calculated for the two-electron pseudo-atom. The integrals (1) involved in this case are elementary and they lead to the analytic expression<sup>5</sup>:

$$R_k = \{ [ 2(Z-2)^{1/2} Z^{1/2} ] / ((Z-1)^{1/2} [ Z^{1/2} + (Z-2)^{1/2} ]) \}^k \quad (2)$$

where  $Z$  is the pseudo-atomic nuclear "charge"<sup>4</sup>. From (2) we may conclude that as expected<sup>3</sup> the differences of the charge distribution of the exact and H-F wf increases when we go away from the nucleus.

TABLE I

Expectation values of  $r^n$   $n = 2, 1, -1, -2$  for the He atom

Operator	$r^{-2}$	$r^{-1}$	$r$	$r^2$
H-F expectation value*	11.991	3.374	1.854	2.370
Exact value*	12.035	3.377	1.859	2.387
Relative Error	.37%	.07%	.24%	.23%

Let us go back, however to the atomic case and take the He atom case where the highly accurate wf of Peckeris<sup>7</sup> provides reliable expectation values. In Table I we present the H-F and Peckeris expectation values with the percentual error for the operator  $r^n$  with  $n = -2, -1, 1, 2$  (see ref. 7). We note that not only  $r^{-1}$  is better depicted using H-F wf than  $r^{-2}$  (which weighs the near-nuclear region more heavily) but also that  $r^{-1}$  has an exceptionally good H-F expectation value. Note that  $r^{-1}$  is precisely the analytical form of the common Coulomb potential.

We can check that the corresponding operator for harmonic oscillator forces, i. e.,  $r^2$  gives also a comparatively exceptional H-F value. This is evident from (2). Yet taking  $Z = 3$  (which is the lowest "nuclear charge" compatible with a stable two-electron pseudo-atom), this value is very poor compared to the exact case, giving an error of over 10%. So in both problems, the atomic and pseudo-atomic systems, the power of  $r$  which coincides with that of the corresponding potential gives a better H-F value than the other

\* Taken from Sahni and Krieger (see ref. 7)

powers. On the other hand the  $\langle r^{-1} \rangle$  error in the atom is a small fraction (.07%) of the energy error (1.2% for He)<sup>2</sup> while the  $\langle r^2 \rangle$  error in the pseudo atom is much larger than the error of the total energy which is 3.4% in this case<sup>4</sup>. In the next section we shall proceed to show how these effects can be expected from the virial theorem for the respective potentials<sup>6</sup>.

### III. HARTREE-FOCK ERRORS AND THE VIRIAL THEOREM

The role of the virial theorem in the calculation of H-F expectation values for ground and excited states of different pseudo-atoms has been discussed by Novaro and Calles<sup>6</sup>. Recently an independent rederivation of some of these results for the two-electron ground state case has been carried out by Lantham and Kobe<sup>8</sup> who compared H-F values with those of other independent particle schemes (this was also done previously by several authors<sup>9</sup>).

TABLE II

Expectation values for the two-electron pseudo-atom energy terms

Operator	Kinetic Energy	Total Potential Energy	Common Attractive Potential	Repulsive Interaction
H-F expectation value <sup>†</sup>	2.121	2.121	3.182	-1.061
Exact value <sup>†</sup>	2.049	2.049	3.549	-1.5
Relative Error	3.4%	3.4%	10.3%	29%

<sup>†</sup> Taken from Novaro and Calles (see ref. 6)

The most relevant aspects of these calculations for our present purposes are contained in Table II where the H-F and exact expectation values for the different components of the two-electron  $Z = 3$  pseudo-atomic hamiltonian are given<sup>6</sup>. The percentual errors are closely related to the virial theorem. The most evident and obvious effect is the fact that the kinetic and total potential energy operators give of course exactly the same H-F error as the total energy (3.4%). The relative error of the repulsive interaction is very large as H-F functions account for only about 70% of the exact value. This is not surprising as the repulsion in this case  $[-\frac{1}{2}(r_1 - r_2)^2]$  is much more dominant than in the atomic problem. In fact what is surprising is that an independent particle scheme as H-F does not in fact imply larger errors for all the operators discussed above. Lantham and Kobe<sup>8</sup> in fact note that other independent particle functions are much poorer for these expectation values. On the other hand they show that this situation is reversed for the common potential  $r^2$ . They attribute this to the poor long range behaviour of H-F functions as is also implied in the conclusions of refs. 5 and 9.

We shall here prefer to invert the argument. As discussed in ref. 6 it is the combined effect of the virial theorem and the optimization of the total energy which implies the huge error in the  $r^2$  H-F value. In fact we are optimizing an operator, the hamiltonian, with important two-body contributions in the potential interaction. The H-F scheme grossly *overcalculates* the common attraction introducing a compensating effect for the error in the value for the repulsion, so that a reasonable expectation value for the other operators linked by the virial theorem turn out to be reasonable. Thus the errors in the total, potential and kinetic energies are not large, but the prize is paid by the error in  $\langle r^2 \rangle$  which implies in turn that the H-F function will give poor values for operators that weigh the outer region of the system.

An analogous situation would arise in atomic systems only when inter-electronic repulsions are comparatively dominant so it is not expected in He. But as the attraction grows with  $n$  (number of electrons) and the repulsion with  $n(n-1)/2$  for large atoms H-F functions may be poor in the region far from the nucleus<sup>3</sup>. In any case this is indeed true for the case of  $H^-$  which exceptionally among He-like ions gives some very poor H-F values. Compare particularly the H-F values for  $r^2$  in He and  $H^-$  as reported by Sahni and Krieger (see ref. 8). This  $r^2$  H-F error changes from 0.24% to 18% from He to  $H^-$  showing that when the repulsion is important the H-F wave functions are deformed mostly in their outer region.

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## RESUMEN

En este trabajo se discuten los valores de expectación de Hartree-Fock para operadores de una sola partícula comparándolos con los valores exactos. Se analizan tanto resultados de la literatura para átomos, como valores calculados en sistemas modelo muy simples, mostrando que las tendencias generales que comunmente se presuponen, efectivamente existen, pero que en muchos casos hay importantes excepciones para algunos operadores. Dichas excepciones están relacionadas a algunas características bien definidas de las funciones de Hartree-Fock, que a su vez provienen del comportamiento analítico de los potenciales en cuestión y a aspectos generales tales como el Teorema del Virial y la coexistencia de operadores de uno y dos cuerpos en el hamiltoniano. Todos estos aspectos se combinan para producir amplificaciones o reducciones en los errores de los valores de Hartree-Fock para algunos operadores.