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THE PSEUDO ATOM: A DISTORTED IMAGE OF ATOMIC SYSTEMS

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ABSTRACT: The so-called Pseudo-Atom, a completely solvable many-body model system, is analyzed by studying the analytical properties of its exact, as well as some independent-particle effective Hamiltonians (as the Hartree, Hartree-Fock, HFA, etc.) and also the correlation potentials. The attractive and repulsive potential operators are plotted and compared with the corresponding potentials, for atoms to show when and how calculations on the pseudo-atom model can provide relevant information for the atomic physicist. It is shown that important differences between physical systems and the model exist,

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permitting us to explain some apparently paradoxical results obtained before and also to predict how a given approximation technique will fare when applied to the pseudo-atom. The general conclusion reached is that to make relevant predictions for atoms, starting from pseudo-atomic calculations, great care must be taken to asses how the peculiar characteristics of the model will deform the information. Then, one can confidently draw conclusions for atoms by reconstructing the deformed image given by the pseudo-atom.

I. INTRODUCTION

One of the most distinguishing and striking characteristics of Prof. Moshinsky's many scientific contributions is indeed, the great amount of relevant information that he obtains using the most transparent ideas and models. He usually makes simple ideas go a long way to provide profound physical insight as, for instance, his masterful use of the simplest dynamical system of all, the harmonic oscillator, in problems ranging from nuclear to classical physics.

To many of us who have had the chance to work with Prof. Moshinsky, his clarity of mind is always related with his relentless push in pursuit of a coherent logical scheme. Even the least trigonometrical relation is always rederived by Moshinsky rather than rely on memory or books. One even feels at first that he wastes time until one realizes that the only waste is in an iddle mind, and that a permanently active and inquisitive mind is the most precious weapon in research. This is not the least of the many lessons we have to thank Prof. Moshinsky for.

The pseudo-atom, a completely solvable many-body system designed to test the approximation techniques of atomic physics, bears these Moshinsky marks. It was developed with the intention of providing a very simple model of atomic structure and rapidly used to test a great many different approximation schemes. At present we can say that this simple, yet non-trivial model system, has been thoroughly employed to extract numerical information about how approximation techniques, as diverse as Hartree-Fock (H–F) perturbation theory, many-electron theories and many others, work.

We thus feel that the time for making straightforward calculations in the pseudo-atom has passed. We need now deeper insight on how and when a technique tested in the pseudo-atom will give relevant information for the atomic physicist. We shall show here that the pseudo-atom gives a defomed picture of atomic behaviour, the amount of deformation depending on what aspects of the pseudo-atomic system are touched by the method being tested.

This is the cause of some apparently paradoxical results that sometimes have been observed in the pseudo-atom. By a careful analysis of the analytical properties of pseudo-atoms as compared with real atoms, we shall be able to explain such "paradoxes" and even predict where pseudo-atomic results will follow closely the atomic ones, where they will grossly exaggerate them and where they will in fact show a behaviour exactly opposite to that in atoms.

We shall start our analysis by taking a second look into the previous results for the accuracy and characteristics of the various independent particle schemes in the pseudo-atom (Sect. II). Then we shall proceed (Sect. III) to do the same for correlation effects, paying special attention to the analytical properties of the different interactions (exact, Hartree-Fock (H-F) correlation, etc.) and their influence in numerical results (Sect. IV). Finally (Sect. V) a statement of our point of view conceming the future use of the pseudo-atom is given.

II. HOW GOOD IS THE HARTREE-FOCK APPROXIMATION AFTER ALL?

Here we shall discuss the different independent- particle schemes, particularly the Hartree-Fock self-consistent field (H-F) and the so-called HFA. This last name is given to independent-particle wave function (wf) with a single adjustable parameter $\overline{Z}$. We shall show that for the pseudo-atom, the energy values of HFA and H-F wavefunctions (wf) are relatively close and also that the H-F energy expectation is not too far from the exact energy. In spite of this, we will find that HFA wf are highly deformed and their overlap with H-F wf is poor and that the H-F wf themselves have poor overlaps with exact wf and are, consequently, very inadequate to calculate reliable expectation values for operators (even one-electron operators) other than the total pseudo-atomic hamiltonian. The fact that independent-particle (HFA or H-F) wf gave relatively good energy predictions but were worse for other properties has long been known[1-3], while previous comparisons between HFA and H-F seemed to indicate that they were very similar[3]. These comparisons were unfortunately mistaken as they were based in a wrong value for the H-F and HFA wf overlap.

First, we will proceed to revise the comparison between HFA and H-F solutions, then we shall compare the independent particle wf with the exact wf, but carefully noting when our conclusions for the pseudo-atom case are extendable to atoms, and where they are no more than a consequence of the pseudo-atom peculiarities.

a) Comparison between H-F and HFA.

In ref. 3 the H-F wf were expanded in the HFA basis for the $8e^-$ pseudo-atom (we shall here write the symbol e^- both for electrons and for particles in the pseudo-atom). From this it was concluded that the HFA orbitals took care of almost all of the H-F wf, as the scalar product between the H-F and HFA $1s$ orbitals reported was 99.82%, and between the $1p$ orbitals 99.93% (ref. 3). Unfortunately these results were wrong and in fact, if used to obtain the H-F energy this would lie above the HFA value, an absurd result. The correct values for the scalar products are: between the H-F and HFA $1s$ orbitals 97.69% and between the $1p$ 99.96%. It is interesting to see that for the $1s$ case the HFA orbital is a rather poor approximation of the H-F one, for $1p$ it is very good, even better than reported in ref. 3. The H-F energy obtained with this correct wf is 22.86, being lower of course than the HFA value 23.238 (ref. 3). The percentage energy error of HFA with respect to H-F is not large and equals 1.65%. On the other hand the product between the complete H-F and HFA wf is only 95.22%.

We shall proceed to discuss those two questions, namely:

i) Why is the $1p$ H-F orbital well depicted by HFA while the $1s$ is not?

ii) Why does the HFA cope well with energy estimations and, in spite of this (or rather, as we shall see below, *because* of this), is poor for other properties such as overlaps, expectation values, etc.?

But first let us analyze another "paradoxical" result of HFA predictions. Let us compare the exact and HFA solutions for three states of the two-e^- pseudo-atom, the ^1S and ^3P ground states (analogous to atomic para- and orto-helium) and the first excited singlet state ^1P. In Table I we give the percentage energy error as well as the scalar product between the complete wf and the orbital scalar products for these states. It should be noted that in the singlet cases ^1S and ^1P the HFA is in fact also the H-F solution while for ^3P the real self-consistent H-F would be expected to lower the energy and overlap errors. But the striking result in Table I is that HFA gives a *better* product with the exact wf for the ^1S state than for the ^1P but that the energy error is *larger* in ^1S than in ^1P states.

TABLE I

Energy percentage error $(E_{\mathrm{HFA}} - E_{\mathrm{ex}})/E_{\mathrm{ex}}$, scalar product $<\psi_{\&\%}, |\psi_{\mathrm{ex}}>$ between the total function and between individual orbitals (1*s* and 1*p*) for the ^1S, ^1P and ^3P states for $2\text{-}e^-$ pseudo-atoms discussed in text.

Pseudo-atomic $2e^-$ State	Percentage HFA Energy Error	Total Scalar Product <HFA|Ex>	1*S* Orbital Scalar Product	1*p* Orbital Scalar Product
^1S	3.5%	97.03%	98.50%	------
^1P	2.91%	96.32%	96.95%	99.35%
^3P	3.79%	96.27%	98.65%	97.59%

All of the above mentioned "paradoxical" results are direct consequences of the way a HFA wf is optimized. The adjustable parameter $\overline{Z}$ is a "shielded nuclear charge" parameter, but the amount of shielding is merely a function of the number of electrons (n) and of the quanta of the state ($N(n)$), and is given by:

$$\overline{Z} = Z - n + (3n/2)[N(n) + 3n/2]^{-1} = 1 + (3n/2)[N(n) + 3n/2]^{-1},$$

the second equality coming from the usual convention $Z = n + 1$. Thus $\overline{Z}$ depends solely on the number of quanta $N(n)$. This implies that the ^1S state has little flexibility to adjust to an optimal energy value as it has $N(n) = 0$. On the other hand to optimize the ^1P state, $\overline{Z}$ is basically given by the 1*p* orbital. Therefore we conclude that the 1*p* orbital will be quite reasonably depicted in the HFA but the 1*s* orbital will be deformed, a prize paid in the HFA to get the best possible energy without a flexible enough wf. This of course explains the difference in the 1*s* and 1*p* overlaps between HFA and H-F orbitals for the $8e^-$ case discussed above.

b) Effect of the Virial Theorem on the H-F Charge Distribution

As we have seen, HFA can be noticeably deformed with respect to true self-consistent H-F wf in spite of the relatively close energy predictions of both. Now we will show that this is also true when comparing the H-F wf with the exact one, a fact that was recognized from the start[1, 3]. More recently it has been shown that many H-F expectation values for one-e^- operators are remarkably poor[4, 5]. In particular the H-F expectation of the pseudo-atom's own common attractive potential usually has a larger percentage error than the total hamiltonian[4].

The origin of this is the very poor expectation value of the two-body repulsion $-\frac{1}{2}(r_1 - r_2)^2$ given by H-F wf. As the repulsive and attractive potentials are linked with each other and with the kinetic and total energies by the virial theorem, we have that to keep the H-F errors in the total, kinetic and potential energies, within reasonable bounds, the common attraction is grossly miscalculated[4, 5]. All H-F values for the r_i^2 terms are much lower than the exact ones. Thus, the H-F expectation values for operators that weigh heavily the tail region of the wf, will be wrong by a huge amount[5]. The concentration of the H-F cloud near the "nucleus" is confirmed by previous analyses of pseudo-atomic form factors[3, 4]. In contrast, we have the atomic case, whose H-F form factors are very similar to the exact form factors, and where the H-F expectation value of the common attraction $1/r_i$ is exceptionally accurate[5].

The different form that the virial theorem takes for a system of particles interacting through Coulomb or oscillator forces implies that, in the first case, the H-F value for the kinetic term is a lower bound to the exact one, while in the pseudo-atom it is an upper bound. Löwdin[6] explains the atomic situation as follows: independent-particle wf allow electrons to get too close together, thus predicting too much repulsion. When exact wave functions, or functions which allow for some e^- correlation are used, electronic movements are complicated by the tendency to avoid each other. As in general we expect that the more constrained the e^- movement is, the higher the kinetic energy will be, we see that the H-F kinetic energy will always be *lower* than the exact value. The pseudo-atomic picture is radically different as concerns the kinetic energy, even if it is still true that the H-F wf permits the e^- to come too close to each other, thus giving less (negative) repulsion and making the total H-F energy an upper bound. But this hardly affects the error in the H-F kinetic term, which only depends on the fact that the H-F wave cloud is much too concentrated in a small region near the nucleus, thus implying that the H-F kinetic energy is an *upper* bound to the exact one.

From the above discussion one gets the impression that to discuss correlation effects in atoms, one has to take into account the instantaneous collisions between e^-, while in pseudo-atoms, correlation effects are more smoothed out as collective effects that affect all the terms in the hamiltonian. This will be substantiated in the following section by analyzing the correlation potential.

III. CONTRAST BETWEEN ATOMIC AND PSEUDO-ATOMIC CORRELATIONS

The most interesting use of the pseudo atom is, by far, the analysis of the different techniques of building correlated wf for atoms. In a sense, the sui-generis behaviour of the H-F wf depicted in the previous section, would only be a curiosity as long as many-e^- effects in pseudo-atoms would resemble closely the atomic situation. It is particularly in analyzing correlation effects where the atomic physicist needs a guide to asses how the different approximation techniques really work.

While very interesting comparisons between these approximations in the pseudo-atom have appeared in the literature[3, 7] showing reasonable behaviour and convergence properties, it is nonetheless true that no critical pre-examination of the analytic properties of the pseudo-atom potentials was done. In our mind, the moment to analyze the *model* has come. No further interpretation of the results is justified if its limitations and scope are not given. We, therefore, would like to address ourselves to answering the question: which of the results come from the qualities and failures of the techniques themselves, and which from the peculiarities of the pseudo-atom? In this section we shall try to disentangle both aspects, noting wherefrom the "paradoxes" arise, and where "good predictions" come from cancelation of errors.

a) Fluctuation Potential for Atoms

In his first paper[8] on many-electron theory (MET) of atoms O.Sinanoglu introduced the so-called fluctuation potential as the difference between the H-F and exact hamiltonian as:

$$H_{\text{ex}} - H_{\text{HF}} = \sum_{i>j} \left[(1/r_{ij}) - \overline{S}_i(j) - \overline{S}_j(i) \right] \equiv m_{ij} \ , \tag{1}$$

where $1/r_{ij}$ is the Coulomb repulsion and $\overline{S}_i(j) + \overline{S}_j(i)$ are the usual H-F potentials containing a direct and exchange part:

$$\overline{S}_i(j) = <\varphi_i(x_i)\,|\,(1/r_{ij})\,|\,\varphi_i(x_i)> - <\varphi_i(x_i)\,|\,(1/r_{ij})\,|\,\varphi_j(x_i)> \; ; \quad (2)$$

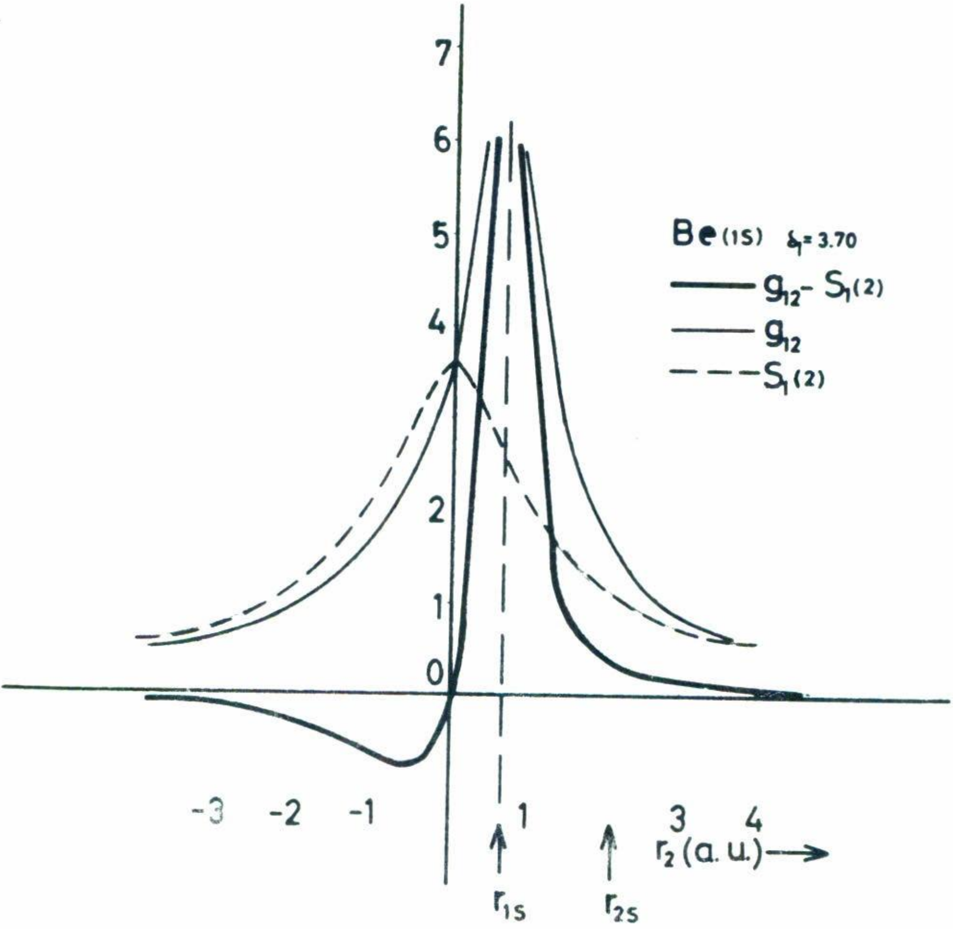

Fig. I. Fluctuations potential for Be atoms as seen by electron at $r_2(e^- 2)$ due to electron $1s(e-1)$ with opposite spin instantaneously at its Bohr radius (r_{1s}). The nucleus, r_1 and r_2 are in the same line. The thin graph is the Coulomb repulsion $g_{12} \equiv 1/r_{12}$ (a.u.). The dashed graph is $S_1(r_2)$ the Hartree-Fock potential of $e^- 1$ acting on $e^- 2$, the heavy graph is the fluctuation potential $g_{12} - S_1(r_2) = m_{12}$. Taken from ref. 8 in text.

here φ_i, φ_j are H-F orbitals. Thus m_{ij} gives the correlation between the e^- that the H-F scheme has neglected and replaced by a central field. Therefore, the m_{ij} will act as a perturbation on the H-F basis set to convert them into the exact solutions. But even without entailing the whole perturbative analysis, the inspection of the analytic form of m_{ij} permits one to visualize how correlation will modify the original H-F solutions. In Fig. I, we reproduce Sinanoglu's[9] plot of m_{ij} as a function of r_{12} for the case of the $1s$ and $2s$ e^- (opposite spins) for the Beryllium atom. The $1s$ e^- is considered as a point particle located in its most probable position (the Bohr radius for Be), and the position of the $2s$ e^- is allowed to vary radially. Note that in Fig. I we are superposing the $\varphi = 0^\circ$ and $\varphi = 180^\circ$ planes, thus giving negative values of r_{2s}.

Three main properties of m_{12} are apparent in Fig. I. First, the singularity in the position of e^- $1s$. This comes from the averaged character of the H-F potential which cannot reproduce the $1/r_{12}$ singularity. Second the fact that m_{12} introduces a small attraction at the opposite side of the nucleus. The third very important fact is the short range of m_{12} contrasting with both the H-F and Coulomb potentials long-range character.

This short range of the fluctuating correlation was interpreted by Sinanoglu as indicating that it was very unlikely that three or more e^- would "collide" simultaneoulsy. So he predicted that pair correlations would dominate, a fact used in most theories of atomic correlations, such as MET, diagram techniques, geminals, etc.

b) Residual Potential in Pseudo-Atoms

Let us now pass to analyze the corresponding situation in the pseudo-atom. In Fig. II we present the m_{12} potential between the $1S$ and $1p$ electrons. The H-F repulsive potential is obtained by definition from the instantaneous repulsion $-\frac{1}{2}(r_1 - r_2)^2$ as

$$-\tfrac{1}{2}\left[r_2^2\int\psi_{1s}^2(r_1)\,dV_1 - 2r_2\cdot\int\psi_{1s}^*(r_1)\,r_1\psi_{1s}(r_1)\,dV_1 + \int\psi_{1s}^*(r_1)\,r_1^2\psi_{1s}(r_1)\,dV_1\right] . \tag{3}$$

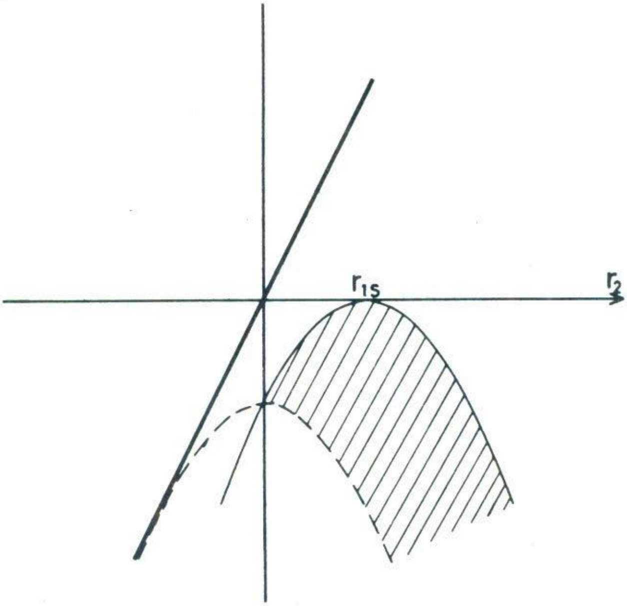

Fig. II. Residual potential for $\overset{+}{\mathrm{Be}}$ pseudo-atom as seen by the *1p* "electron" (e^-2) with position r_2 due to the 1s e^- at its most probable position r_{1s}. The thin graph is $-\frac{1}{2}(r_1 - r_2)^2$ the dashed graph is H-F repulsion of e^- 1s acting on e^- *1p*, the heavy graph is the residual potential m_{12}.

The first integral is 1 by normalization and the second one vanishes from parity considerations, so we finally have that the H-F repulsion (see Fig. II) is simply:

$$-\tfrac{1}{2}\,(r_2^2 + \langle r_1^2 \rangle) \;; \tag{4}$$

the correlation operator corresponding to Sinanoglu's fluctuation potential, which we shall call the residual pseudo-atomic correlation, is therefore:

$$m_{12} = -\tfrac{1}{2}\,(r_1^2 - 2r_1 \cdot r_2 + r_2^2) + \tfrac{1}{2}\,(r_2^2 + \langle r_1^2 \rangle) \;. \tag{5a}$$

that is,

$$m_{12} \approx (r_2 \cdot \langle r_1 \rangle) = \text{constant} \cdot r_2 \;,$$

because in Fig. II we are fixing the 1s e^- at $r_1 = \langle r_1^2 \rangle$.

From eq. 5 and Fig. II we see that the H-F repulsion is merely the $-\frac{1}{2}(r_1 - r_2)^2$ term displaced down and centered in the origin, while m_{12} is a straight line that passes through the origin and goes to $+\infty$ in the side of the nucleus where the 1s e^- is, ($\varphi = 0°$) and to $-\infty$ in the opposite side of the nucleus ($\varphi = 180°$). The H-F repulsions are not too different, analytically, near the origin for the atomic and pseudo-atomic problems, as Fig. III shows. But as H-F reproduces the $1/r_{12}$ tail reasonably, as seen in Fig. I, (implying short-range correlations in atoms), in Fig. II there is a long-range catastrophe as the H-F and exact repulsion are increasingly differing as we go away from the nucleus. The residual pseudo-atomic correlations have infinitely long-range. As this residual potential is the one that corrects the deffects of the H-F wf, it is evident that we can expect a very poor asymptotic behaviour of the H-F wf. This explains the enormous errors in the expectation values of operators that weigh the outer region of the H-F charge cloud[5].

From the above discussion we would expect a dramatic change in many-electron correlation effects in the pseudo-atom as compared with the

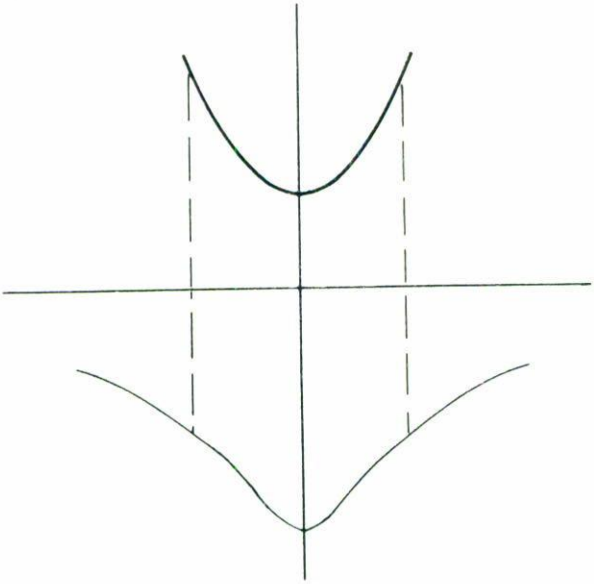

Fig. III. Comparison between the H-F repulsion for atoms (see Fig. I) and for pseudo-atoms (see Fig. II). Notice that in the region near the origin they are quite similar, except for the obvious difference in sign atom. In ref. 7 MET was tested in the 4-e^- pseudo-atom and it was concluded that simultaneous pairs still took into account most of the correlation energy. How can this be understood in the light of the long range of m_{ij} in pseudo-atoms?

There are two parts to the answer. Let us first take a closer look to the results of MET in the 4-e^- pseudo-atoms[7]. First of all, single pair correlations account for only 40% of the correlation, simultaneous pairs for another 40%, therefore leaving an error of 20% which must come from simultaneous three- and four-body collisions. This is much more than would be expected in atomic calculations[8] but, as the authors note[7], it is to be expected in the pseudo-atom system where repulsive effects are so dominant. In view of the above discussion we could rephrase this justification by saying that the residual potential is by far more prone to many-electron collisions than the short-range fluctuation in atoms.

We now analyze why three- and four-body collisions are not, in fact, even more important than they are, in spite of the very long-range character of the m_{ij}'s.

IV. PAULI'S PRINCIPLE, THE FERMI HOLE AND EXCLUSION EFFECTS

a) The Fermi Hole and Approximate Exchange

The effect of the exclusion principle on H-F wf for atoms has been thoroughly discussed in the literature[6]. A pictorial way to describe how the antisymmetry affects the independent particle wf, is to say that each e^- carries a hole, the Fermi hole, that surrounds the e^- in question and which consists of a deficiency of charge of the same spin, amounting to a total of, one e^- charge. The main difference between the Hartree and H-F schemes is the way in which they correct the repulsion that its own charge cloud exerts on each e^-. In the Hartree scheme this self-repulsion is just subtracted out of the spherically averaged electron cloud, while in the H-F method the Fermi hole follows the e^- movement, thus keeping all other e^- with the same spin a safe distance away. Thus, Löwdin[6] draws two main conclusions about the effect of the Fermi hole on the H-F energy: i) it will be considerably better than the Hartree value and, ii) it will practically erase all correlation effects coming from electrons with *equal* spins, as the Fermi hole erases their charge near the electron in question, exactly where the fluctuating potential is more important[8] (see Fig. I).

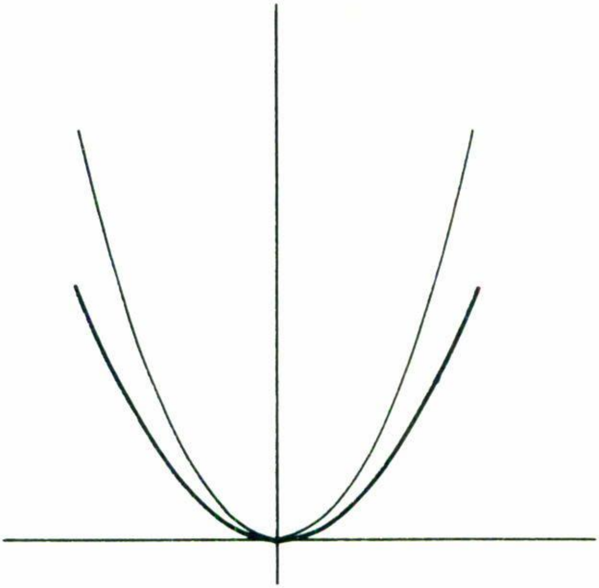

Fig. IV. Comparison between the parabolae of the Hartree and HFA common attractive potentials for the triplet ground state ^3P of the 2-e^- pseudo-atom. The HFA parabolae (heavy graph) is wider than the Hartree parabolae (thin graph) because its effective charge is smaller: $\overline{Z}_H = Z - {}^3\!/_4$ for Hartree, $\overline{Z}_{HF} = Z - {}^5\!/_4$ for HFA.

As it concerns the pseudo-atom conclusion i) is valid: the Fermi hole effectively lowers the Hartree energy.

In fact the most obvious difference between Hartree and H-F (or HFA) is the considerable broadenning of the parabolae of the common attraction in HFA, as compared with Hartree (see Fig. IV). This comes from the smaller effective nuclear charge $\overline{z}$ in HFA. This effect alone is enough to account for a more diffuse HFA electronic cloud and a lower HFA energy referred to Hartree solutions. Take, for instance, the percentage energy errors given by Hartree for the two-e^- triplet ground state ^3P, and four-e^- all spins equal pseudo-atoms, that are, respectively, 17.7% and 17.3% and compare with the HFA errors of only 3.8% and 7%, respectively. The Fermi hole is also effective in the pseudo-atom in reducing the deformation of the HFA orbitals. This can be seen from Table I where the two-e^- states ^1P and ^3P show a different behaviour. As discussed in Section II for the singlet state, the $1s$ orbital is highly deformed while the $1p$ is not. In the triplet state, the Fermi hole averages the situation treating the $1s$ and $1p$ states more equitatively.

In the pseudo-atom, however, the second effect of the Fermi hole, proposed by Löwdin is not present. This means that the correlation effects of e^- with parallel spins will be just as important as for antiparallel spins. Take the ^3P two-e^- state which has as large a correlation energy as the ^1S or ^1P states. Or the 4-e^- with all spins equal, with 7% correlation energy.

This important difference in pseudo-atomic and atomic behaviour can be understood by the comparative analysis of Figs. I and II. In the atomic case, the effect of the Fermi hole between the $1s$ and $2s$ (parallel spins) electrons is to forbid the $2s$ e^- to go near the position where the other is. This means that the Fermi hole is in fact playing a role closely similar to that of the Coulomb hole itself. Thus the region where the fluctuating potential is important, is a forbidden region for all e^- with spins parallel to the $1s$ e^-[8] (see Fig. I).

In the pseudo-atomic case, on the other hand, even if the Fermi hole does erase charge from the region where the H-F potential has spuriously let too much charge into (shaded area in Fig. II), this is far from being critical as concerns the residual potential which dominates in the region farthest removed from the nucleus. So the Fermi hole has hardly taken into account any e^- correlation, in marked contrast with the atomic situation.

The image of the Fermi-hole, guided Slater[9] to introduce an approximate local potential that would replace the non-local exchange term in H-F equations. The idea is to subtract one electron charge from the total H-F density around the point where the moving electron is. This is equivalent to removing a charged sphere whose radius is determined from:

$$4/3\,\pi r_0^3 \rho = e \tag{6}$$

$$r_0 = [(3e/4\pi)\rho^{-1}]^{1/3} \tag{7}$$

where ρ is the density of e^- charge of the same spin as that of the moving electron, which will notice the effect as an attraction that a uniformly charged sphere of radius r_0 would exert on it. Thus it will be attracted by a force $1/r_0$ or $\rho^{1/3}$. Slater consequently proposed the replacement of the exchange term in H-F by a $\rho^{-1/3}$ attraction[9].

The equivalent situation in the pseudo-atom would imply the substitution of the exchange term by a function of the density which, using Slater's method, turns out to be[10] a function of $\rho^{-2/3}$.

It is very interesting to note that, while it is quite natural to have the exponent $-2/3$ (remember that the potential is here proportional to r^2 or $\rho^{-2/3}$), the exponent's negative sign implies weighing the *low density* regions of the H-F cloud, thus giving preeminence to the region where $\left| r_1 - r_2 \right|^2$ is large. The actual calculations using the local exchange $\rho^{-2/3}$ are being carried out.

b) The Exclusion Effect in Many-Body Collisions

Sinanoglu has shown that even in those cases in atomic physics where three electrons are radially close, as for instance the Boron ground state $(1s)^2\,(2s)^2\,2p$ where the last three e^- are all in the L shell, the exclusion effect acts to prevent the possibility of the three e^- colliding simultaneously. We shall show here that the same conclusion is reached in the

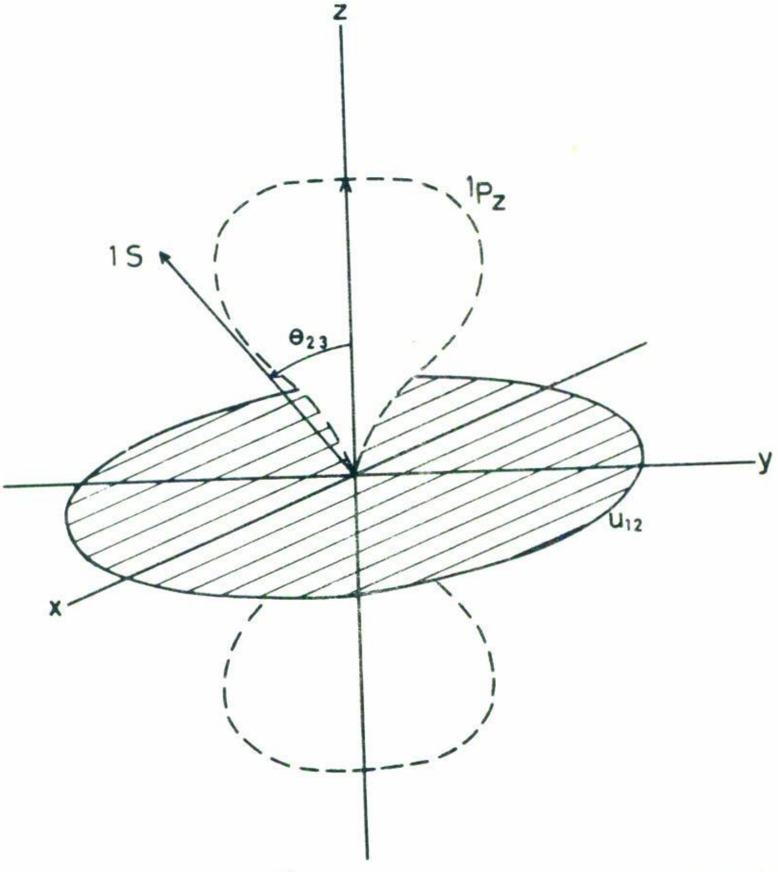

Fig. V. Exclusion effect in the $\overset{+}{Be}$ pseudo-atom (1s 1p), due to the $2p_z$ "electron" (e-3) located at its most probable position (see its position vector in z-axis). The $1s^2$ correlation u_{12} is confined to the vicinity of x-y plane because it is orthogonalized to orbital 1p.

case of the pseudo-atom in spite of the evident differences between the fluctuating potential in atoms (see Fig. I) and the residual potential in pseudo atoms (see Fig. II).

In Fig. V we show the $1p$ probability density projected on the YZ plane with the $1p$ e^- located at the point of maximum probability, another electron ($1s$) at the same fixed radial distance from the nucleus is allowed to modify its position by varying the relative angle θ_{23} depicted in the figure. In Fig. VI we reproduce the fluctuation potential as a function of the angle θ in the Boron atom as given in ref. 8. Fig. VII depicts the same for the residual potential for the $(1s)^2\, 1p$ pseudo-atom. Despite the difference between the potentials in Figs. VI and VII, the general conclusion[8] obtained from both is the same and it comes mainly from the fact that the m_{ij} potential vanishes at $\theta = \pi/2$, the xy plane of Fig. V.

Let us rederive Sinanoglu's arguments and the conclusions for the case of the pseudo-atom. In the $1s^2\, 1p$ *state the first two* $1s$ e^- can correlate through the pair function u_{12} which is largely composed of three degenerate $(1p)^2$ determinants that contain the $1p_x$, $1p_y$ and $1p_z$ orbitals and which

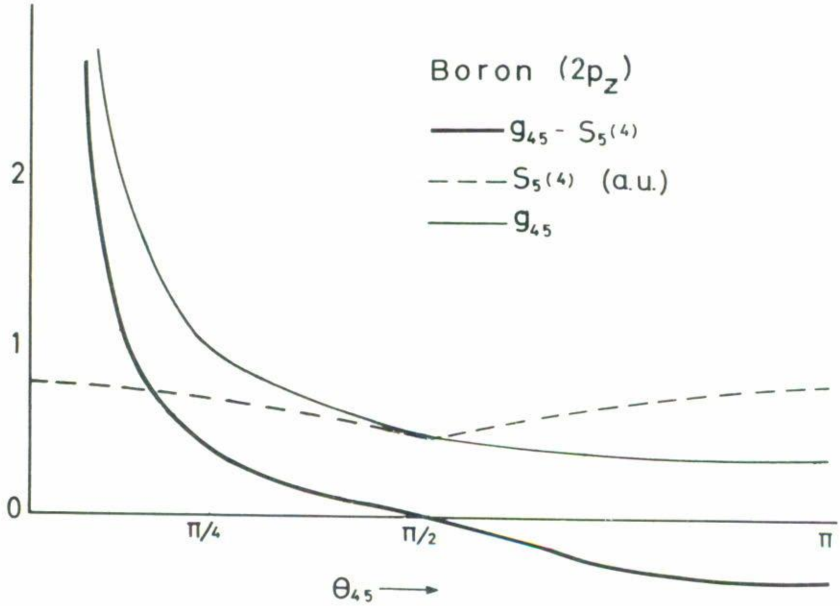

Fig. VI. Exclusion effect in Boron atom. The fluctuation potential (heavy graph) is seen by e^-4, in a state $2s$, due to e^-5 at the maximum of ^2p_z. Thin graph depicts Coulomb repulsion $g_{45} \equiv 1/r_{45}$, dashed line $S_5(4)$ is H-F repulsion of e^-5 acting on e^-4, both e^- at same radial distance from nucleus. Taken from ref. 8 in text.

are the dominant correlations in the Configuration Interaction analysis of the exact wf in the two-electron $1s^2$ pseudo-atom. By MET we have that for the $(1s)^2\,1p$ pseudo-atom, we must orthogonalize u_{12} with respect to $1p_z$, so the main part of u_{12} is concentrated in a disk in the xy plane (the shaded disk of Fig. V). As shown in Fig. VII, it is precisely in this plane that the potential m_{23} vanishes. As u_{23} will only be important where the residual potential m_{23} is large, we have that the product $u_{12}u_{23}$, which is responsible for triple collisions, is everywhere small, i.e., u_{23} is vanishingly small just where u_{12} is not negligible (xy-plane) and viceversa. This (or rather

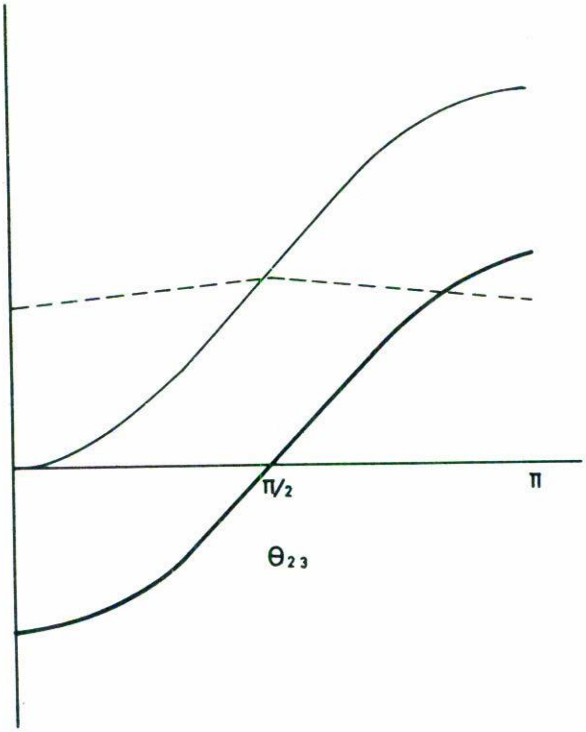

Fig. VII. Exclusion effect in Be^+ pseudo-atom. The residual potential (heavy graph) as seen by e^-2 (in 1s state) due to e^-3 located in $2p_z$ ***maximum*** (as in Fig. V). The thin graph is the $-\frac{1}{2}(r_1 - r_2)^2$ repulsion and the dashed graph the H-F repulsion. Note that here, as in Fig. VI the correlation potential is always zero at $\theta = \pi/2$, the xy plane of Fig. B. One should note that even if for closed shell atoms the H-F potentials are spherically symmetric, in open shells they are slightly deformed. We see that in fact H-F has here minima at $\theta_{45} = 0$ because the $1p_z$ orbital is the only occupied p-state (see Fig. V). In Fig. VI H-F had maxima at $\theta_{23} = 0$ and π for exactly the same reason the corresponding situation for atoms), was called the exclusion effect by Sinanoglu[8], and answers the last question raised in section III, namely, why in spite of the long-range behaviour of the residual potential three-, four- and more-e^- collisions are not too important, even if they contribute substantially more to the correlation effects than in the atomic case.

V. OUTLOOK AND CONCLUSIONS

Rather than repeating here the particular conclusions already discussed in the preceeding sections about the different approximation techniques tested in the pseudo-atom, let us instead try to establish an outlook towards the future. Our general philosophy here is that no further "blind" calculations on the pseudo-atom are justified any longer.

This does not imply however that we deem the pseudo-atom worthless as a testing ground for approximation techniques, but rather that one should carefully choose the problem, where it can give relevant information. Thus the calculations of H-F or equivalent expectation and transition values, specially for electromagnetic operators, seem worthless in a system where one-electron operators, such as the system's own common potential, are so poorly given by independent-particle functions. Also great care must be taken with further tests of correlation theories for many-e^- pseudo-atoms because, as discussed above, many-body correlations are much more important than in the atomic case. In fact, we can predict from the analysis of the residual potential of Fig. II, that simultaneous correlations involving more than two particles will be more and more important as the total number of particles increases. Atomic correlations behave quite differently. This may result in a disguised blessing, however, as our completely solvable model may be used to estimate many-body terms by diagrammatic field theoretic techniques, for instance. These results would be interesting for systems where collective effects (as in liquid Helium) or long-range correlations (as in crystals[8]) imply many-body excitation from the H-F sea. Of course any prediction, about crystals, for instance, (with nearly free e^-), would have to take into account the overwhelming differences between the model system and the physical one. But as we have shown throughout this paper, this is also true in the case of atoms. So much so, that we suggest that the name pseudo-atom should be omitted and with it the fiction of minimal ionization ($z = n + 1$) which just exaggerates the divergences between atomic and pseudo-atomic correlation effects. Perhaps a better convention is to take $z = 2n$, since in atoms correlation errors are of the order of 1% for all atoms[6]. Thus the usefulness of this solvable many-body system will lie in its careful use to test the mathematical devices and its judicious comparison with physical systems. A previous estimation of how will the physical picture be altered in the model in each case is necessary.

We shall thenceforth be in a much better position for carrying Moshinsky's program of making relevant predictions about atomic behaviour starting from our model system. Such predictions will result from the careful addition of the various bits of information given by the pseudo-atom , like the reconstruction of an image reflected by a distorting mirror.

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RESUMEN

El sistema modelo de muchos cuerpos, totalmente soluble, llamado pseudo-átomo, es analizado a través del estudio de las propiedades analíticas de su hamiltoniano exacto así como las de algunos hamiltonianos efectivos de partícula independiente (tales como Hartree, Hartree-Fock, HFA, etc.) y también los potenciales de correlación. Los potenciales atractivos y repulsivos se graficaron para compararlos con los potenciales correspondientes en el caso atómico para mostrar cuándo y cómo se puede obtener, a partir de cálculos en el pseudo-átomo, información relevante para el físico atómico. Se muestran algunas diferencias notables entre los sistemas físicos y el modelo, lo cual permite explicar algunos resultados previos aparentemente para-

dójicos y también predecir qué tan buenas predicciones puede dar una técnica de aproximación dada cuando se aplica el pseudo-átomo. La conclusión general es la siguiente: para poder hacer predicciones acertadas para átomos a partir de cálculos pseudo-atómicos, debemos ser extremadamente cuidadosos y estimar cómo las características peculiares del modelo afectarán la información. Sólo entonces podremos extraer con confianza las conclusiones aplicables al caso atómico, procediendo a reconstruir la imagen deformada que el pseudo-átomo provee.