Correlation study of endohedrally confined alkaline-earth-metal atoms (A@C_{60})

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Correlation Study of Endohedrally Confined Alkali Earth Atoms (A@C_{60})

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The effects of endohedral confinement on the correlation energy of Be, Mg, and Ca atoms have been investigated using modified Hartree-Fock (HF) and multiconfiguration Hartree-Fock (MCHF) methods where the endohedral system (A@C_{60}) is approximated as an atom enclosed in an attractive spherically symmetric potential well of inner radius $r \sim 5.8$ a.u. and thickness of $\Delta \sim 1.89$ a.u., and correlation energies are studied as a function of the depth of the confining potential ($0 \leq U_0 \leq 1$ a.u.) to give some idea as to how the correlation energy behaves in different endohedral environments. In general, we have found that, as a function of well depth, starting from the free atom, valence electrons diffuse outward, in the presence of the confining potential, which causes the electrons to be further apart, thereby decreasing the correlation energy; however, with further increase of well depth, the valence electrons become trapped in the confining well and, as a result of their being closer together, the correlation energy increases.

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I. INTRODUCTION

Endohedral atoms are of increasing interest in physics and other fields because the confined atoms exhibit a variety of new and unique features which are relevant to a broad range of possible applications [1–4]. In addition, the study of the properties of endohedral atoms offers a "laboratory" to investigate the effects of confinement on atomic structure and transitions, and a large number of studies of these properties are extant [5, 6]. Correlation in various forms have been found to be important, or even determinative, in many cases. A useful measure of correlation, at least in bound states, is the correlation energy which is defined as the difference of the exact energy of the state and the independent particle, Hartree-Fock (HF) [7], energy. The exact energy can be well-approximated by a multiconfiguration Hartree-Fock (MCHF) [8] approach in which case, the correlation energy of an atomic system is defined approximately as

$$E^{corr} = E^{MB} - E^{HF}$$

where E^{HF} is the Hartree-Fock energy, the energy calculated within a single-configuration description of the atom and, E^{MB}, the MCHF energy, is obtained including many-body correlations.

In the present investigation, we focus on the ground state of the alkali earth atoms Be, Mg and Ca and calculate the correlation energy for the free atoms compared to the confined atom in an attractive spherically-symmetric potential with various well-depths of the confining potential to simulate a variety of confining environments. These atoms were chosen for a number of reasons. They are closed-shell atoms, which simplifies the calculation. In addition, the closed-shell nature of these atoms means that the interaction with the inner wall of the confining shell will be only through a van der Waals interaction, i.e, very weak [9]. Furthermore, previous work has shown that neutral Li, Mg and Rb are in stable equilibrium at the center of the C_60 shell, so it seems reasonable that Ca might be as well [9]; this is not true of alkali earth positive ions, which were found to be in equilibrium off-center [9]. And, in fact, this work shows that an a neutral alkali earth atom which is off-center would be pushed back to the center where the energy is a minimum. In any case case, for atoms residing in the canter of the cage, treating the interaction as a central potential seems to be a reasonable approximation. Lastly, the binding energies of the valence ns subshell is much less than the $(n\text{-}1)p$ inner subshell, so that we can learn about the effects of confinement on correlation for both diffuse and compact wave functions. The calculation does not include Rb or Ba because they are heavy enough that relativistic effects would be at least as important as correlation and we are performing explicitly non-relativistic calculations.

II. THEORY

In our studies, the endohedral environment is approximated with a short range spherical potential, $V_{ext}(r)$,

$$V_{ext}(r) = \begin{cases} -U_0 & r_c \leq r \leq r_c + \Delta \\ 0 & \text{otherwise} \end{cases}$$

where the inner radius of the potential r_c= 5.8 a.u., the thickness of the well is Δ = 1.89 a.u. U_0 = 0.302 a.u., which corresponds to confinement by C_{60} [10]. To make the results more general, we have investigated the response of atom to the depth of the confining potential as a crude way to model a variety of confining situations.

In atomic units, the Hamiltonian of an N-electron atomic system, confined by the above potential, is given by

$$\mathcal{H} = \sum_{i=1}^{N} \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + V_{ext}(r_i) \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \ .$$

The energy of atomic system is obtained from the expectation value of the Hamiltonian, $<\Psi|\mathcal{H}|\Psi>$, where $|\Psi>$ represents either the single configuration HF wave function or MCHF wave function. For the case where $V_{ext}(r) = 0$, the details and procedures for obtaining these wave functions are dealt with extensively in the literature, e.g., see Chap. 4 of Ref. [8] and references therein. To perform this study with the addition of the confining potential we have modified Froese Fischer's latest MCHF atomic structure codes [7] by adding $V_{ext}(r)$ potential to the direct atomic potential. These codes were originally designed to work with the free atomic systems in a logarithmic radial mesh points, where the densities of radial mesh points are decreasing in the large-r region. In general, outer-shell orbitals become more diffuse in confined atoms [11, 12], therefore we further needed to modify the code to use a finer radial mesh to represent the diffuse orbitals better and account for the effect of the external well potential more precisely. All one-electron orbitals are then calculated within a self-consistent method in the same way the free-atomic orbitals are obtained [8]. Note that the methodology and codes that were used in this study are specifically aimed at a spherically symmetric potential, a potential that does not depend upon angle. In other words, the methods are applicable only if the atom is situated in the center if the C_{60} shell.

In order to avoid any numerical difficulties that may arise from including a step-like potential with sharp edges, the edges of $V_{ext}(r)$, the external potential, are smoothed by using a Wood-Saxon potential [13] to approximate our model potential. The form of Wood-Saxon potential is

$$V(r) = -\frac{V_0}{1 + exp(\frac{r-R}{\gamma})} \qquad (1)$$

where γ is known as the surface thickness parameter and is a measure of diffuseness of the edge region of the potential. In this work, the edges of the $V_{ext}(r)$ are smoothed with a surface thickness parameter $\gamma = 0.1$. The smoothed $V_{ext}(r)$ potentials are shown at the modified radial mesh points for four different well depths in Fig. 1. The diffuse, rather than sharp edge regions of the potentials abnegate any possibility of unphysical effects owing to a discontinuity in the potential. However, it has been found in a previous study of photionization of confined atoms [14] that such effects are minuscule. In addition, in the present study, we have found only tiny effects of the changing the diffuseness of the potential.

III. RESULTS AND DISCUSSION

A. Correlation in Beryllium

The MCHF energy of the $1s^2 2s^2$ state is calculated using 17-LS terms obtained by considering all possible double-promotions (and couplings) from $1s$ and

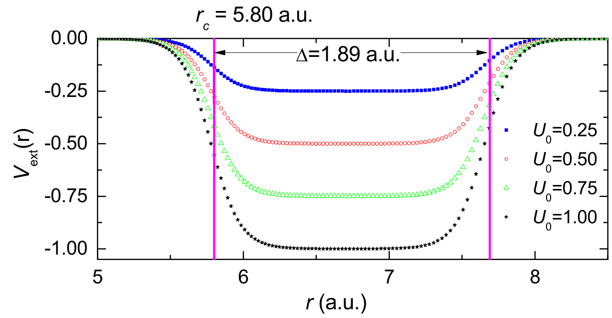

FIG. 1: (Color online) $V_{ext}(r)$ potentials with various U_0 (a.u.) values smoothed using $\gamma = 0.1$ thickness parameter.

$2s$ subshells into $2p$, $3s$, $3p$, and $3d$ correlation orbitals; specifically $1s^2 2s^2$, $1s^2 2p^2$, $1s^2 3s^2$, $1s^2 3p^2$, $1s^2 3d^2$, $1s^2 2p3p$, $2s^2 2p^2$, $2s^2 3s^2$, $2s^2 3p^2$, $2s^2 3d^2$, $2s^2 2p3p$, $1s2s2p^2$, $1s2s3s^2$, $1s2s3p^2$, $1s2s3d^2$, $(1s2s)^1S2p3p$ and $(1s2s)^3S2p3p$. For free Be, the result of the MCHF calculation is -14.651173 a.u. Note that this energy is quite close to earlier results; -14.665870 a.u. from a 52-term configuration interaction (CI) calculation [15], and -14.667357(8) a.u. from a CI expansion including large number of configurations [16]. Using the same 17 terms in the MCHF wave function, the total energies were calculated for the confined atom in confining potentials of a range of depths; the HF energies were also calculated. The results of both calculations are shown in Fig. 2 where the difference between the two energies (the correlation energy), at each well depth, is evident. It is also apparent from Fig. 2 that the magnitude of the total binding energy increases with increasing well depth. This is, of course, expected since a more attractive potential should result in a greater binding energy. We are, however primarily interested in the correlation energy, and its evolution as a function of well depth; this is shown in Fig. 3.

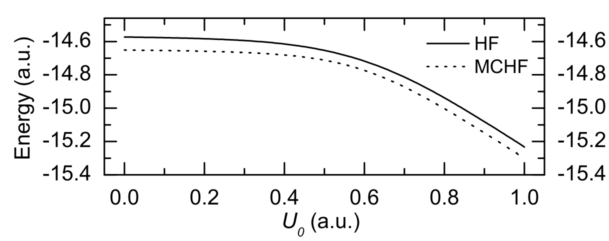

FIG. 2: HF and MCHF total energies of beryllium as a function of the well depth, U_0.

Of particular interest in Fig. 3 is the surprising behavior of the correlation energy; starting from the free atom, the correlation energy gets smaller in magnitude as the strength of the potential well increases up to a certain well depth, and then increases as the well depth increases further. To understand this phenomenology, we first look at the mixing coefficients among the 17-LS terms in the MCHF expansion and note that only the $1s^2 2p^2(^1S)$ configuration interacts significantly with

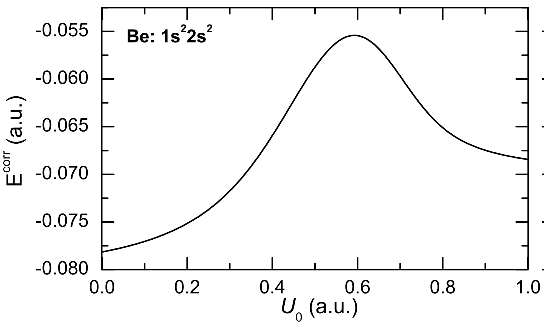

FIG. 3: Correlation energy of confined beryllium as a function of the well depth, U_0.

the $1s^2 2s^2(^1S)$ ground state; our calculation shows that the squares of the mixing coefficients all of the other terms are 0.001 or less. The mixing, as a function of well depth, between $1s^2 2p^2(^1S)$ and $1s^2 2s^2(^1S)$ then is shown in Fig. 4, where it is seen that this mixing follows the same pattern as the correlation energy; decreasing from the free atom with increasing well depth, and later increasing. The explanation for this behavior can be traced to the $2s$ and $2p$ orbitals themselves, and these are shown in Fig. 5 for a selection of well depths, U_0.

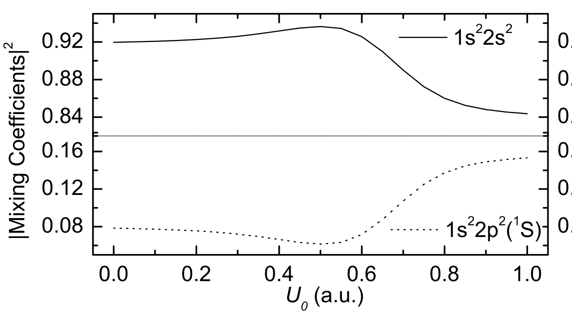

FIG. 4: Squares of the mixing coefficients for $1s^2 2s^2$ and $1s^2 2p^2$ terms in the MCHF expansion for as functions of the well depth, U_0.

Looking at Fig. 5 a number of features emerge. First, for all well depths studied, from the free atom to U_0 =1 a.u., the spectroscopic $2s$ and correlation $2p$ one-electron radial orbitals overlap appreciably. Second, is that both wave functions are pulled more and more towards the confining well as the well depth increases. And third, when U_0 reached 1 a.u., virtually all of the amplitude of each orbital is confined to the region of the confining well. Thus, starting from the free atom, since the orbitals move to larger r with increasing well depth, the interaction between $2s^2$ and $2p^2$ decreases because the Coulomb interaction goes as $1/r$, i.e, as the well depth increases, the orbitals spread out over a larger volume, making them further apart so that the interaction between the electrons gets smaller. Ironically, at high U_0, where the orbitals get confined in the well, the effective value of r is no longer increasing. What is shown in Fig. 5

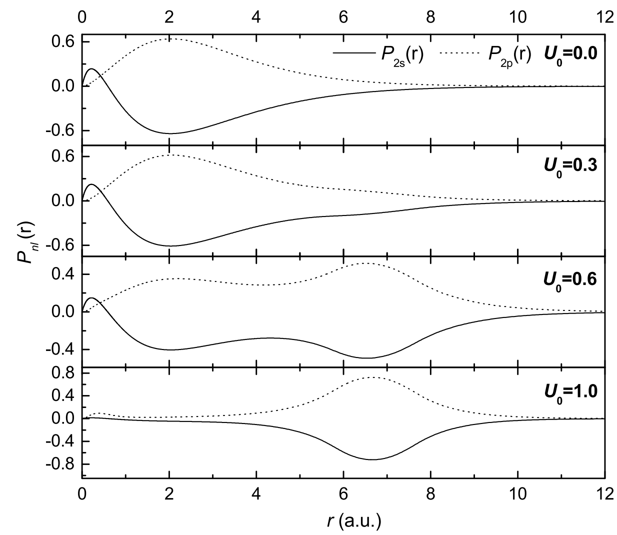

FIG. 5: $2s$ and $2p$ one-electron radial orbitals in Be for a selection of well depths, U_0 (a.u.).

is that as the well depth increases for high U_0, the amplitudes of the orbitals confined in the well increase (see the bottom panel of Fig. 5), i.e., they get closer together, i.e., they occupy a smaller range of r,so that the interaction between the $2s^2$ and $2p^2$ configurations increases (as seen in Fig. 4), leading to the increase in the correlation energy with well depth at high U_0.

B. Correlation in Magnesium

The ground-state energy of Mg including many-body correlation effects is obtained using a slightly different technique than the Be case owing to the existence of four subshells in this case. Specifically, we started with the HF orbitals of the occupied $1s$, $2s$, $2p$, and $3s$ subshells of the Mg ground state. Then we added $3p$, $4s$, $3d$, $4p$, and $4d$ correlation orbitals to the mix and built a wave function as a 73-LS term expansion formed by considering all possible single- and double-promotions from $2s$, $2p$, and $3s$ subshells into $3p$, $4s$, $3d$, $4p$, and $4d$ correlation orbitals; promotions from $1s$ were omitted because their coefficients turn out to be so very small. Then a *restricted* MCHF calculation was performed on the ground state of Mg, restricted in the sense that the HF orbitals corresponding to the occupied $1s$, $2s$, $2p$, and $3s$ were kept fixed, but all of the correlation orbitals were allowed to vary. For the ground-state energy of free Mg, our calculations give -199.865661 a.u. which is even lower than previous,-199.6469 a.u. from a 3-LS configuration [17] and -199.64830 a.u. from 8-LS configurations [18] full-MCHF calculations.

We have found that, as a function of well depth, the correlation energy in Mg, as seen in Fig. 6, is similar to the behavior of Be, discussed above. Note, however, that while the total variation of the correlation energy with well depth is similar to the Be case, the actual values of the correlation energy is four or five times larger in Mg that in Be. The simple explanation for this phenomenology is that much of the correlation energy of Mg comes from the inner $2s$ and $2p$ subshells; and since these subshells are so deeply bound, they are essentially unaffected by the confining well so that their contribution to the correlation energy does not vary with well depth. In other words, only the outer $3s$ subshell really contributes to the *variation* of correlation energy with well depth.

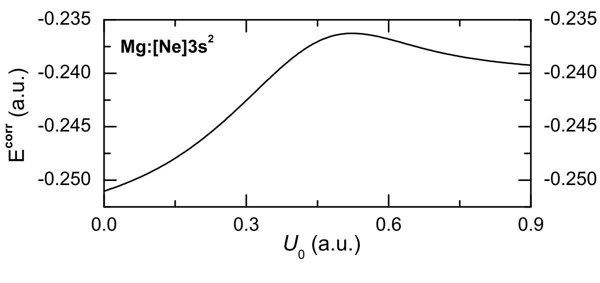

FIG. 6: Correlation energy of ground state of Mg as a function of U_0.

In order to understand the variation of the correlation energy with well depth, we have looked at the mixing coefficients among 73-LS terms in the wave function of the ground state of Mg and we found the strongest mixing occurs between the ground state and the doubly excited [Ne]$4p^2(^1S)$ state, analogous to the situation in Be, and these mixing coefficients as a function of U_0 are shown in Fig. 7.

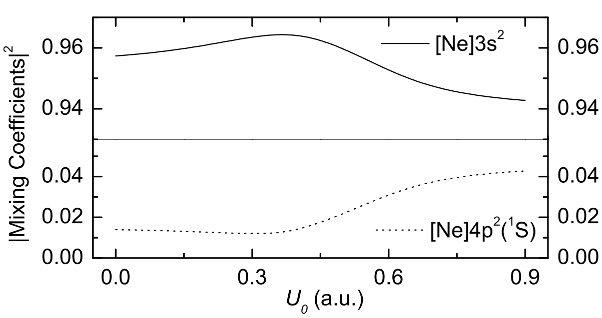

FIG. 7: Dominant mixing coefficient squares in confined Mg as a function of U_0.

As depicted in Fig. 7, the mixing between [Ne]$3s^2$ and [Ne]$4p^2(^1S)$ behaves qualitatively in the same manner as in the Be case; a decrease from the free atom to a minimum as U_0 increases, followed by an increase in the larger U_0 region. To understand this behavior, Fig. 8 shows the $3s$ and $4p$ one-electron orbitals at various U_0 values.

The story here is essentially the same as in the Be case; starting from the free atom, where they are seen to overlap quite well, the $3s$ and $4p$ orbitals densities move to larger r so that they are more spread out and the interaction between them decreases. Eventually, however,

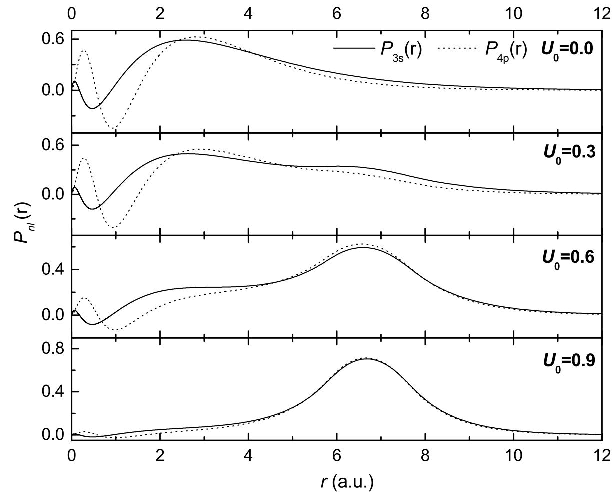

FIG. 8: $3s$ and $4p$ one-electron radial orbitals in Mg with different U_0 (a.u.) .

the are drawn more and more into the confining well as it deepens so that, despite being at a larger r, they get closer together. Note that the primary mixing in of the outer ns^2 subshell in the Mg case is not with np^2, as in the Be case, but with $(n+1)p^2$. However, this arises from the mathematics of the situation and has no physical significance that we can discern. Note also, that the sum of the squares of the coefficients of the two major configurations is about 0.98 (it changes somewhat as a function of well depth), whereas for Be it is almost exactly 1.0. Thus, for Mg, other configurations have become more important, as compared to Be.

C. Correlation in Calcium

The calculation for Ca is done almost exactly like the Mg case; all of the occupied orbilas in the ground state, $1s$ through $4s$, are obtained at the HF level and fixed. Then, a 73-LS term wave functions formed by considering all possible single- and double-promotions from $3s$, $3p$, and $4s$ orbitals into $3d$, $4p$, $5s$, $5p$, and $5d$ correlation orbitals was constructed and the correlation orbitals were determined *via* a restricted MCHF calculation. The resulting ground state energy obtained is -676.980837 a.u which is lower than ,-676.7862 a.u. predicted in a previous calculations with a simpler CI-expansion [17]. Fig. 9 presents the correlation energy in Ca as a function of depth of the well where similar behavior to Be and Mg cases is found.

We have further investigated the mixing-coefficients among 73-LS terms and we found the strongest mixing occurs between the ground state and the doubly excited [Ar]$5p^2(^1S)$ state, just like in the Mg case but with the principal quantum numbers increased by unity. The mixing coefficients as a function of increasing U_0 are shown in Fig. 7 where similar behavior to the previous cases is

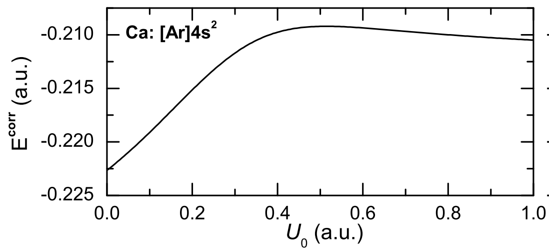

FIG. 9: Correlation energy of ground state of Ca as a function of U_0.

seen, except that the total of the two major coefficients is about 0.95 in this case (again, dependent upon the well depth) which indicates that the lesser terms are becoming still more important.

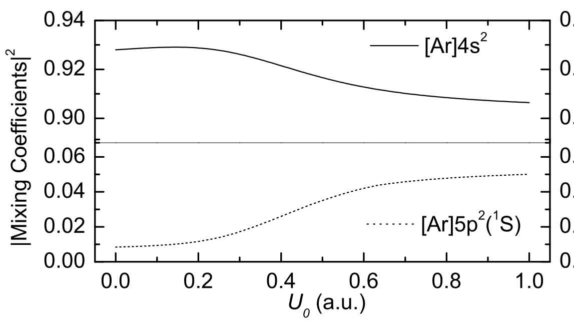

FIG. 10: Dominant mixing coefficient squares in confined Ca as a function of U_0.

Finally, Fig. 8 depicts the $4s$ and $5p$ one-electron orbitals at various U_0 values which illustrates exactly the same behavior as seen in Be and Mg.

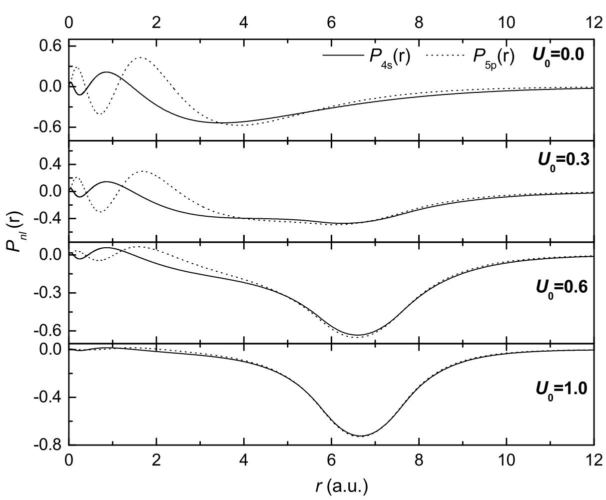

FIG. 11: $4s$ and $5p$ one-electron radial orbitals in Ca with different U_0 (a.u.).

IV. CONCLUSION

This work has shown that correlation effects in endohedrally confined alkali earth atoms, A@C_{60}, with a confining potential of depth $U_0 = 0.302$ a.u. which is derived from experiment, is smaller than in free atoms; the reasons for this phenomenon are explained in terms of the valence orbitals be pulled from their positions in the free atom into the confining well. To understand a larger class of physical situations, calculations were performed as a function of U_0 for the correlation energies of confined Be, Mg, and Ca where unusual behavior was found. Starting from $U_0 = 0$, the correlation energies decrease with increasing U_0 as the outer (ns^2) electron wave functions get more diffuse, an eventually reach a minimum; with the further increase of U_0, the correlation energies increase as the valence (ns^2) electrons get localized in the confining well. This effect is more pronounced for Be, because $2s$ electron is involved with the most of the correlation, while for Mg and Ca the inner-shell electrons account for most of the correlation; however, since these inner-shell electrons are too tightly bound to get pulled into the confining well, their contribution to the correlation is not altered by the confinement.

As a result of these calculations, even on only three atoms, we can make some generalizations for the entire periodic table. Confining wells of the order of the strength involved in entrapment of atoms by fullerenes will strongly affect the properties of the valence levels, but not the static properties of inner atomic shells. Valence orbitals of ground states of atoms will get pulled towards the confining well and, as the well becomes deep enough, get "sucked in." Thus, there are two opposing effects that the confining well can have on valance orbitals, depending upon the strength of the well: moving the probability densities out to larger r, thereby diffusing them and causing them to interact less strongly with each other; and trapping them in the confining well itself which causes them to interact more strongly with each other. As a result of these two opposing effects, the study of the static properties of atoms trapped in a variety of situations should prove most interesting.

Finally, as mentioned earlier, the present study deals with atoms at the center of the cage. However, in many cases the equilibrium position of the trapped atom or ion is off-center [6]. In addition, vibrational and external fields can also cause the trapped atom or ion to stray from its equilibrium position. But, even if the trapped particle strays from the central position, as long as the external potential is spherically symmetric, it will not be attached to the shell because a spherically-symmetric charge distribution exhibits no force in its interior, a simple result of Gauss' law. For off-center atoms or ions however, the calculation becomes very much more complicated because the interaction with the field of the C_{60} is no longer isotropic and orbital angular momentum of the atom is no longer a good quantum number. Such studies would be most interesting; they are, however, beyond the scope of our present capabilities.

V. ACKNOWLEDGMENTS

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