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## LETTER TO THE EDITOR

## A configuration interaction model to investigate many-electron systems in cavities

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### Abstract

A configuration interaction (CI) model to treat confined many-electron systems is presented. Our model proposes a spatially confined linear combination of configuration interaction (LCCI) functions, built from basis functions that do not satisfy confinement boundary conditions. As an application we have calculated total energies for the He ground state, assuming that the atom is enclosed within a spherical cavity with infinite potential walls. Comparisons with other results in the literature are made in order to verify our model.

The problem of a spatially confined system has been subject of interest in many branches of physics and chemistry since the early years of quantum mechanics. In 1928, the problem for an electron in a uniform magnetic field confined by a harmonic oscillator type potential had already been solved by Fock [1], and in 1940, Schrödinger [2] analysed hydrogen-like atoms in a hyperspherical curved space, that is, confined by a cotangent-type potential. At the present time, investigations on confined systems in physics [3–5] have focused especially on the study of artificial atoms, also known as quantum dots (essentially a number of electrons confined in a potential well). In quantum chemistry, the confined models have been used to study a series of chemical phenomena that occur in cavities, such as cages or channels in zeolite molecular sieves [6, 7], adsorption in heterogeneous catalysis [8], and endohedral complexes, such as atoms and ions inside fullerene cages [9–11]. A review by Jaskólski [12] gives a broad account of these studies prior to 1996 and a complete list of later works concerning confined atoms may be found in a very recent paper by Connerade *et al* [13]. An analysis of these studies shows that several of them are concerned with one-electron systems or with many-electron atoms described at the Hartree–Fock level.

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However, a large theoretical motivation for the study of enclosed systems is to understand in detail the electron correlation effects on the properties of those systems. This letter is proposing an approach to determine energy and correlated state functions for confined systems. Our method is based on the variational principle and imposes that a linear combination of configuration interaction (LCCI) functions must vanish at the cavity border via a set of constraint equations for the expansion coefficients. In other words, we represent the confined exact state function as a linear combination of  $N$ -electron trial configuration interaction (CI) functions. We illustrate the method by applying it to CI energies for the helium atom inner spherical box with infinite potential well.

We begin by constructing determinantal functions from the self-consistent field (SCF) orbitals obtained by solving the Hartree–Fock–Roothaan equations for the unenclosed system. Next, we determine a basis set of occupied  $\{\phi_i\}_{i=1}^j$  and virtual (or unoccupied)  $\{\phi_i\}_{i=j+1}^r$ ,  $j < r$ , orbitals and we compose the configuration state functions (CSFs), e.g. Slater determinants  $\Phi_k$  or combinations of them, involving excitations from the occupied to virtual orbitals and satisfying the spin symmetry [14]. With those CSFs we obtain

$$\Psi = \sum_k D_k \Phi_k \quad (1)$$

solutions of the general CI matrix equation

$$HD = ESD \quad (2)$$

where the matrix elements of  $H$ ,  $S$  and  $D^\dagger$  are, respectively,

$$H_{kl} = \int \Phi_k^* H \Phi_l \, d\mathbf{r}_1 \, d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (3)$$

$$S_{kl} = \int \Phi_k^* \Phi_l \, d\mathbf{r}_1 \, d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (4)$$

$$D^\dagger = (D_1^*, D_2^*, D_3^*, \dots) \quad (5)$$

and the Hamiltonian operator is given by

$$H = - \sum_i \sum_A \left( \frac{1}{2} \nabla^2(i) + \frac{Z_A}{r_{iA}} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}}. \quad (6)$$

The solutions of equation (2) give a set,  $\{\Psi_i\}_{i=1}^s$ , of CI-state functions, ground and excited ones, and its corresponding eigenvalues  $E_1, E_2, \dots, E_s$  describing the non-confined system. Hence, we consider these  $N$ -electron functions as a basis set  $B$  in which we expand the confined exact many-electron function  $\tilde{\Psi}$ , i.e. we propose the trial function

$$\tilde{\Psi} = \sum_{j=1}^n C_j \Psi_j \quad (7)$$

with  $\{C_j\}_{j=1}^n$  being a set of variational parameters to be determined under confinement conditions. In fact, as the CI-state functions  $\Psi_j$  ( $j = 1, 2, \dots, n$ ) do not satisfy the confinement boundary conditions, we must impose those conditions on the expansion (7). This is done by applying the linear variation method to the functional  $\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle_c$  inside the confinement region  $\mathbb{C}_\omega$  and satisfying the constraints

$$\langle \tilde{\Psi} | \tilde{\Psi} \rangle_c = \int_{\mathbb{C}_\omega} \tilde{\Psi}^* \tilde{\Psi} \, d\mathbf{r}_1 \, d\mathbf{r}_2 \dots d\mathbf{r}_N = 1 \quad (8)$$

$$\tilde{\Psi}(\mathbf{r}_1 = \mathbf{r}_{(k)}, \mathbf{r}_2 = \mathbf{r}_{(k)}, \dots, \mathbf{r}_N = \mathbf{r}_{(k)}) \equiv \tilde{\Psi}(\mathbf{r}_i = \mathbf{r}_{(k)}) = b_k, \quad k = 1, 2, \dots, m \quad (9)$$

where  $\mathbf{r}_{(k)}$  represents the coordinates  $\mathbf{r}_i$  ( $i = 1, 2, \dots, N$ ) at the  $k$ th boundary of  $\mathbb{C}_\omega$ , and  $b_k$  is the value that the  $\tilde{\Psi}$  takes at this boundary. The index  $c$  indicates the integrals are evaluated inside the region  $\mathbb{C}_\omega$ .

Using the functional  $\langle \tilde{\Psi} | H | \tilde{\Psi} \rangle_c$  and the constraints (8) and (9) we write

$$\mathcal{L}[C_i, \mathcal{E}, \Lambda_k] = \langle \tilde{\Psi} | H | \tilde{\Psi} \rangle_c - \mathcal{E} \{ \langle \tilde{\Psi} | \tilde{\Psi} \rangle_c - 1 \} + \sum_{k=1}^m \{ \Lambda_k [\tilde{\Psi}(\mathbf{r}_k) - b_k] + \Lambda_k^* [\tilde{\Psi}^*(\mathbf{r}_k) - b_k^*] \} \quad (10)$$

where  $\mathcal{E}$  and  $\Lambda_k$  are Lagrange's undetermined multipliers, and so the necessary condition for extremum values of (10) are obtained from

$$\delta \mathcal{L}[C_i, \mathcal{E}, \Lambda_k] = 0. \quad (11)$$

It means

$$\sum_{i=1}^n \delta C_i^* \left\{ \sum_{j=1}^n [H_{ij}^c - \mathcal{E} S_{ij}^c] C_j + \sum_{k=1}^m \Psi_i^*(\mathbf{r}_{(k)}) \Lambda_k^* \right\} + \text{c.c.} = 0. \quad (12)$$

Since  $\delta C_i^*$  is arbitrary, we obtain the set of conditions

$$\sum_{j=1}^n H_{ij}^c C_j - \mathcal{E} S_{ij}^c C_j + \sum_{k=1}^m \Psi_i^*(\mathbf{r}_{(k)}) \Lambda_k^* = 0 \quad (13)$$

and the expansion of  $\tilde{\Psi}$  obeys the constraint equation

$$\sum_{j=1}^n C_j \Psi_j(\mathbf{r}_{(k)}) - b_k = 0. \quad (14)$$

For problems where all of the  $b_k$  are zero (Dirichlet boundary conditions) we have, from (13) and (14), the generalized eigenvalue problem

$$\begin{pmatrix} \mathbf{H}^c & \mathbf{\Psi}^\dagger \\ \mathbf{\Psi} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C} \\ \mathbf{\Lambda}^* \end{pmatrix} = \mathcal{E} \begin{pmatrix} \mathbf{S}^c & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C} \\ \mathbf{\Lambda}^* \end{pmatrix} \quad (15)$$

for which we define

$$\mathbf{\Psi}^\dagger = \begin{pmatrix} \Psi_1^*(\mathbf{r}_{(1)}) & \cdots & \Psi_1^*(\mathbf{r}_{(m)}) \\ \Psi_2^*(\mathbf{r}_{(1)}) & \cdots & \Psi_2^*(\mathbf{r}_{(m)}) \\ \vdots & \ddots & \vdots \\ \Psi_n^*(\mathbf{r}_{(1)}) & \cdots & \Psi_n^*(\mathbf{r}_{(m)}) \end{pmatrix} \quad \mathbf{\Psi} = \begin{pmatrix} \Psi_1(\mathbf{r}_{(1)}) & \cdots & \Psi_n(\mathbf{r}_{(1)}) \\ \Psi_1(\mathbf{r}_{(2)}) & \cdots & \Psi_n(\mathbf{r}_{(2)}) \\ \vdots & \ddots & \vdots \\ \Psi_1(\mathbf{r}_{(m)}) & \cdots & \Psi_n(\mathbf{r}_{(m)}) \end{pmatrix}$$

and  $\mathbf{H}^c$  is the  $n \times n$  Hamiltonian matrix,  $\mathbf{S}^c$  is the  $n \times n$  overlap matrix (here, all integrals are evaluated in the confinement region  $\mathbb{C}_\omega$ ),  $\mathbf{C}$  is the column vector of the coefficients and  $\mathbf{\Lambda}^*$  is the conjugated vector of the Lagrange undetermined multipliers  $\Lambda_i^*$ . However, we should note, as in our procedure the CI basis functions  $\Psi_j$  are chosen to be eigenfunctions of  $H$ , the matrix elements of  $\mathbf{H}^c$  can be calculated as

$$H_{ij}^c = \int_{\mathbb{C}_\omega} \Psi_i^* H \Psi_j \, d\mathbf{r}_1 \, d\mathbf{r}_2 \dots \, d\mathbf{r}_N = E_j \int_{\mathbb{C}_\omega} \Psi_i^* \Psi_j \, d\mathbf{r}_1 \, d\mathbf{r}_2 \dots \, d\mathbf{r}_N = E_j S_{ij}^c \quad (16)$$

where the matrix elements of  $\mathbf{S}^c$  are given, explicitly, by

$$S_{ij}^c = \sum_a \sum_b D_{ai}^* D_{bj} \langle \Phi_a | \Phi_b \rangle_c \quad (17)$$

with each element  $\langle \Phi_a | \Phi_b \rangle_c$  written as

$$\langle \Phi_a | \Phi_b \rangle_c = \int_{\mathbb{C}_\omega} \phi_{a1}^*(\mathbf{r}_1) \phi_{a2}^*(\mathbf{r}_2) \dots \phi_{aN}^*(\mathbf{r}_N) \times \sum_{\mathbf{P}} \epsilon_{\mathbf{P}} \mathbf{P} \phi_{b1}^*(\mathbf{r}_1) \phi_{b2}^*(\mathbf{r}_2) \dots \phi_{bN}^*(\mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (18)$$

and  $\phi_{ai}(\mathbf{r}_i)$  and  $\phi_{bi}(\mathbf{r}_i)$  being single-particle functions which compose the Slater determinants  $\Phi_a$  and  $\Phi_b$ , respectively.  $\mathbf{P}$  is the permutation operator and  $\epsilon_{\mathbf{P}}$  is the parity of the  $\mathbf{P}$ th permutation.

From the formalism above, the non-trivial solutions of equation (15) are obtained solving the determinantal equation

$$\det \begin{bmatrix} H^c - \mathcal{E} S^c & \Psi^\dagger \\ \Psi & \mathbf{0} \end{bmatrix} = 0 \quad (19)$$

which is a polynomial equation of order  $(n - m)$  in  $\mathcal{E}$ , i.e. the total energy for the confined many-electron systems. In addition, as our space is restricted to the confined region  $\mathbb{C}_\omega$ , the Hamiltonian matrix elements must be made symmetric by replacing  $H_{ij}^c$  by  $\frac{1}{2}(H_{ij}^c + H_{ji}^c)$ .

The computational effort to implement our model for confined many-electron systems requires, initially, an ordinary CI calculation (full or truncated) for the unenclosed system in order to obtain a basis set  $B$  of state functions, which composes the trial confined state function  $\tilde{\Psi}$ . In this letter we have solved the full CI problem for the helium atom through the ground and first excited states generated with the so-called 6-311G atomic basis set [15, 16]. Therefore, our trial function is chosen to be composed of two eigenfunctions of the Hamiltonian  $H$  corresponding to the unenclosed atom. If we choose the confinement region as being a sphere of radius  $r = R$ , there exists only one constraint equation, i.e.  $\tilde{\Psi}(R) = 0$ . Thus, equation (19) becomes

$$\begin{vmatrix} H_{11}^c - \mathcal{E} S_{11}^c & H_{12}^c - \mathcal{E} S_{12}^c & \Psi_1^*(R) \\ H_{21}^c - \mathcal{E} S_{21}^c & H_{22}^c - \mathcal{E} S_{22}^c & \Psi_2^*(R) \\ \Psi_1(R) & \Psi_2(R) & 0 \end{vmatrix} = 0 \quad (20)$$

where  $H_{ij}^c$  and  $S_{ij}^c$  are given, respectively, by (16) and (17). Due to spherical symmetry, the evaluation of  $S_{ij}^c$  is simple, with all of them reducing themselves to a linear combination of integrals of the general form

$$\int_0^R \exp(-\alpha r^2) r^2 dr. \quad (21)$$

We have calculated the total energies,  $\mathcal{E}$ , of the helium atom placed at the centre of spheres with different radii,  $R$ . The results are compared with two different methods in the literature [17, 18], as shown in table 1. In the first method, developed by Gimarc [17], the author has used a state function which includes some radial correlation. Such a function is multiplied by a cutoff factor and gives a value of  $-2.8757$  Hartrees for the total energy of the helium ground state at  $R = \infty$ . The second method has been proposed by Ludeña and Gregori [18] and requires a previous Hartree-Fock (SCF) calculation with atomic basis functions also multiplied by cutoff factors. In this case the authors have used an atomic basis set which includes s-, p- and d-functions, and have obtained an energy of  $-2.9025$  Hartrees for the ground state of the non-confined helium atom. On the other hand, our method does not require cutoff factors in the functions, i.e. it is not necessary that the basis functions satisfy confinement boundary conditions. Here, it should be noted that our basis functions  $B$  are chosen as eigenfunctions of the Hamiltonian  $H$  in all regions of space. To illustrate the method for the confined helium atom, we have considered, as explained above, the basis

**Table 1.** Energy in Hartrees of the confined  $\text{He}(^1S_0)$  atom in a spherical box of radii  $R$  (au). Our results are obtained by using a LCCI composed of two full-CI states generated with the 6-311G basis set.

$R$	This paper (LCCI results)	Ref [17]	Ref [18]
1.30	-1.5495	-1.1924	
1.40	-1.6011	-1.5792	-1.6156
1.50	-1.6914	-1.8692	
1.60	-1.8250	-2.0891	-2.1250
1.70	-1.9954	-2.2576	
1.80	-2.1814	-2.3876	-2.4230
1.90	-2.3567	-2.4887	
2.00	-2.5028	-2.5678	-2.6026
2.20	-2.6947	-2.6791	
2.40	-2.7902	-2.7491	
2.60	-2.8358	-2.7936	
2.80	-2.8570	-2.8222	
3.00	-2.8684	-2.8407	-2.8708
4.00	-2.8764	-2.8716	-2.8988
5.00	-2.8764	-2.8755	-2.9020
$\infty$	-2.8764	-2.8757	-2.9025

set  $B$  formed by two CI-state functions  $\{\Psi_1, \Psi_2\}$ , generated by the usual atomic basis set 6-311G [16]. For the unenclosed helium atom, the eigenvalues of these CI functions are, respectively,  $E_1 = -2.8764$  and  $E_2 = -1.5249$  Hartrees. Then, we have used equation (7) for  $n = 2$  and solved equation (20) to obtain the energies of the confined system. Our results are in agreement with both methods cited above [17, 18], although the nature of the confined functions and methodologies are different. For instance, while the other authors have utilized Slater functions in their calculations, we have used Gaussian functions. It is well known in the literature that Gaussian functions, far from the core, are more contracted in comparison with Slater functions [19], and therefore they are less sensitive to the variations of the cavity radius for some values of  $R$ . Our energy values are influenced by this property of the atomic basis set: they are highly increased near the core, whereas for larger values of  $R$  the energy converges quickly for the non-confined value. Such behaviour can be analysed in table 1, where it is observed that LCCI energies increase slightly for a cavity with radius larger than 2.40 au. It is also seen in table 1 that our values (notice the energy differences between two consecutive values) are more sensitive to the compression in the range from 1.60–2.00 au, in comparison with values presented by Gimarc [17] and Ludeña and Gregori [18].

In summary, we have presented in this letter a theoretical procedure to study confined many-electron systems. This procedure is a generalization of the formalism of linear variation basis functions that do not satisfy boundary conditions proposed by Goodfriend [20] for one-electron systems. As its main advantage, our methodology does not require calculations of two-electron integrals in the cavity, while in the cited methodologies [17, 18] these integrals should be modified due to introducing a cutoff factor in the basis functions, which is necessary to fulfil the confinement boundary conditions. In this context, the proposed model is general and may be applied to many-electron confined systems since the state functions describing the corresponding unenclosed system are given. Our intention in the present letter has not been to obtain the best energy for the confined helium atom at the full CI

level. Our numerical results can be improved by adding higher angular momentum functions to the atomic basis set; the addition of atomic functions improves the CI-state functions, i.e. the basis set  $B$ , and in consequence the energy values obtained from equation (20) for the enclosed system become better. Instead, we are interested in presenting a feasible solution to the confined atomic problem through a new formalism. In particular, the procedure presented here could be used to understand the nature and physical significance of many-body effects in confined electronic systems, such as artificial atoms, for example. Work in this direction is in progress and the results will be presented in a forthcoming paper.

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