

CORRELATED STATES
FOR ATOMS AND ATOMIC CLUSTERS:
A COMBINED EXACT DIAGONALIZATION
— *AB INITIO* APPROACH*

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We have proposed a novel method (EDABI) of approach to nanoscopic correlated systems that combines an exact diagonalization method with an *ab initio* readjustment of the single-particle orbitals. With the help of this method we study correlated electronic states of atoms and small clusters. In the case of atomic systems with $Z < 10$ we can perform the analysis of the ground- and excited- states systematically improving the accuracy of the calculation. For the two- and three- dimensional clusters containing up to $N = 4$ atoms the electronic and lattice properties are analyzed as a function of interatomic distance. Three- and four- site interactions are included for simple s-like orbitals. With an increasing interatomic distance the Hubbard gap appears already for the cluster systems.

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We present results for light atoms and H_4 clusters within the recently proposed by us method combining an exact diagonalization of Hamiltonian of interacting particles in the Fock space with an *ab initio* optimization of the single-particle orbitals in the ground state (EDABI). The results illustrate the feasibility of the method when applied to *the correlated states* of small quantum dots and clusters.

An exact solution of interacting (correlated) electronic systems incorporating an *ab initio* procedure in a consistent manner, is important even for model systems. This is because we obtain the properties of a system of correlated electrons as a function of lattice parameter, not only as a function of interaction parameters, as is usually the case. In this respect, our

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group has devised recently [1–3] *a novel method of approach* involving both an exact treatment of the interparticle interaction expressed in the Fock space by the Hamiltonian diagonalization in the occupation-number representation, combined with a readjustment of single-particle wave functions contained in the microscopic parameters. It should be underlined that the wave-function optimization takes place *only after* the interaction has been included in the ground-state-energy expression. In the situation when this optimization of the ground-state-energy is carried out variationally, our method represents a variant of the full multiconfiguration-interaction method with self-consistently adjusted orbitals (MCI-SCF method [4]). The only approximation in our method is the finite size (and thus, its incompleteness) of the single-particle basis defining the field operator (and thus the *reduced Fock space*).

TABLE I

Optimized Bohr-orbit size of $1s$, $2s$, and $2p$ orbits (in units of a_0), the overlap S between renormalized $1s$ and $2s$ states, and the ground state energy for the lightest atoms and ions.

	a_{1s}	a_{2s}	a_{2p}	S	E_G (Ry)
H	1	2	2	0	-1
H ⁻	0.9696	1.6485	1.017	-0.1	-1.0487
He	0.4274	0.5731	0.4068	-0.272	-5.79404
He ⁻	1.831	1.1416	0.4354	-0.781	-5.10058
Li	0.3725	1.066	0.2521	0.15	-14.8334
Be ⁺	0.2708	0.683	0.1829	0.109	-28.5286

In the present contribution we test the effectiveness of our method by first calculating the ground and first excited (not displayed here) states characteristics of simple atoms and ions (H⁻, He, Li, He⁻ and Be⁺) and small cluster of $N \leq 4$ H atoms in various configurations. The role of electronic correlations is crucial, as we will discuss in detail next. In Table I we provide the variationally optimized radii of the $1s$ (a_{1s}), $2s$ (a_{2s}), and $2p$ (a_{2p}) orbitals of wave functions composing the orthogonal (molecular) single-particle basis. We see that the Bohr-orbit sizes a_n differ substantially from that of hydrogen (it is measured in units of $1s$ Bohr radius $a_0 \simeq 0.53\text{\AA}$). The corresponding ground-state energy in each case is not far away from the corresponding exact values (the quantitative test will be discussed separately).

In Table II we provide the principal characteristics representing the mixing of the single-electron states in the situation when the interaction between them is included. The columns represent respectively: the hopping t between orthogonalized (Wannier) $1s$ and $2s$ states, as well as the interaction parameters in the orthogonalized basis: the (Hubbard) interaction

amplitudes between $1s$ (U_1), $2s$ (U_2), $2p_0$ (U_3) and $2p_{\pm 1}$ (U_p) states, the interactions $1s$ – $2s$, $1s$ – $2p$, and $2s$ – $2p$ (K_{12} , K_{13} , and K_{23} , respectively). Those parameters represent a sizable fraction of the ground-state energy and determine the admixture of higher excited states to the ground state (*e.g.* the admixture of $1s$ – $2s$, $1s$ – $2p$, *etc.* configurations to the $1s^2$ atomic state). It should be emphasized that those parameters are needed when setting the quantum electrodynamics of the atom.

TABLE II

Microscopic parameters (in Ry) of the selected atoms and ions all quantities are calculated for the orthogonalized atomic states.

	t	U_1	U_2	U_3	U_p	K_{12}	K_{13}	K_{23}
H [−]	0.057	1.333	0.369	0.77	0.728	0.519	0.878	0.457
He	1.186	3.278	1.086	1.924	1.821	1.527	2.192	1.289
He [−]	−1.1414	1.232	0.764	1.798	1.701	0.929	1.421	1.041
Li	−0.654	3.267	0.533	3.105	2.938	0.749	3.021	0.743
Be ⁺	−0.929	4.509	0.869	4.279	4.049	1.191	4.168	1.175

We now turn to the small planar and 3D clusters of 3 or 4 hydrogen atoms taking into account only a single $1s$ state per atom. In the case of molecular physics of this type the electron correlations effects arise because the intraatomic (intrasite) interactions can become larger than single-particle (the particle-hopping) energy, particularly at a larger interatomic distances, the last being regarded as an experimentally controllable parameter. In Fig. 1 we display the ground state energy per atom of clusters with N atoms and for several arrangements. One sees that the H₂ molecule is the most stable state and hence the $N = 3$ and 4 clusters can be stabilized only on *e.g.* surface, *i.e.* when the additional trapping potential is present. It is also intuitively understandable why the planar configuration of $N = 4$ atoms is the next stable one. Namely, it is closer to two H₂-molecules configuration than the spatial (tetrahedron) H₄ arrangement.

In obtaining Fig. 1 two factors are important [5]. First, the Slater $1s$ orbitals were taken and orthogonalized to define the field operators and, more importantly, the Hamiltonian representation in the Fock space, subsequently brought to the diagonal form with the help of modified Lanczos procedure. Second, 3- and 4-site interaction terms in the atomic representation were estimated by demanding that they vanish in the orthogonalized (Wannier) and optimized representation.

Probably the most interesting feature of the present cluster calculations is the structure of the levels displayed here in Fig. 2 for $N = 4$ planar case. Namely, with the increasing distance R the energy manifolds split up into well defined groups corresponding to the Hubbard subbands. The middle

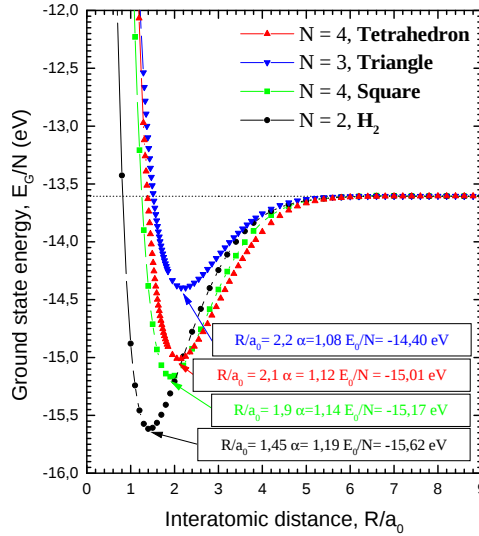


Fig. 1. Ground state energy per atom as a function of interatomic distance (in units of $1s$ Bohr radius), for several clusters of N atoms. The characteristics: the distance R at minimum energy, the inverse size (α) of the optimized $1s$ orbit, and the value of E_G at minimum, are listed explicitly in each case.

subband, representing the states with a double atom occupancy (energy excess $\sim U/4$ per atom for the first higher subband). Actually, this subband is split into two because there is a slight difference depending on the configuration of the remaining two electrons. The highest state in energy for this cluster is that with two double occupancies. However, this state contains as many empty sites (we have $N = 4$ with 4 electrons), so the third subband is not so well defined as the second. We therefore see that the principal feature of many-body structure — the Hubbard subbands — appears already in molecular systems. This result is possible to achieve in a clean form only when we study a systematic evolution of the system as a function of the lattice parameter.

In conclusion, it is of fundamental importance to extend the present results to larger N to see systematically the development of extended (solid-state) state from molecular (cluster) states. Also, an implementation of the method in Gaussian basis would make it possible to perform the analysis for various systems such as fullerene, transition-metal clusters and other cases. Furthermore, one should compare the present results with those obtained from commercially available codes.

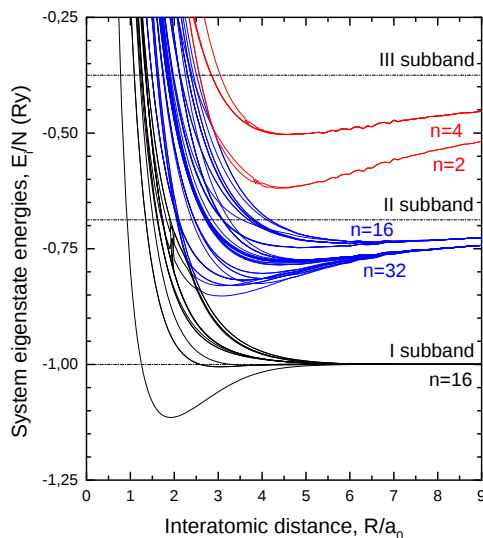


Fig. 2. Energy levels of $N = 4$ square cluster *vs* R . Note the splitting into the Hubbard subbands with the increasing R .

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