APPLICATION OF THE GAUSSIAN TIME-DEPENDENT HARTREE METHOD TO THE STUDY OF THE GROUND STATE OF NEON CLUSTERS

APLICACIÓN DEL MÉTODO DE HARTREE GAUSSIANO DEPENDIENTE DEL TIEMPO AL ESTUDIO DEL ESTADO BÁSICO DE CLUSTERS DE NEÓN

A. R. Ramos-Ramos[a†], L. Uranga-Piña[a] y A. Martínez-Mesa[a]

DynAMoS (Dynamical processes in Atomic and Molecular Systems), Faculty of Physics, University of Havana, Cuba. arramos@fisica.uh.cu
† corresponding author

Recibido 20/3/2016; Aceptado 24/5/2017

The ground state properties of neon clusters are studied through the Gaussian Time-Dependent Hartree (G-TDH) method. The presence of significant quantum effects in these systems poses a significant challenge to its theoretical investigation, because it drastically reduces the number of atoms that can be simulated in a computer. The application of the G-TDH method alleviates this difficulty, and it allows to study the ground state properties as a function of cluster size without neglecting the quantum effects. The method is based on the construction of an approximate wavefunction for the whole system, consisting in a Hartree product of normalized single-particle wavepackets of Gaussian shape. These Gaussian functions are characterized by their widths, and their centroids in position and momentum spaces. Using the Dirac-Frenkel-McLachlan variational principle and the imaginary-time propagation technique, we obtain the equations of motion that describe how these parameters approach the values that better describe the ground state of the system, and they enable to synthesize the system wavefunction of the system and to compute the structural and energetic properties of the cluster in the ground state.

Se estudian las propiedades del estado básico de *clusteres* de neón mediante la aplicación del método de Hartree dependiente del tiempo utilizando paquetes de onda gaussianos (G-TDH, por sus siglas en inglés). La presencia de efectos cuánticos significativos en estos sistemas representa un importante desafío para las investigaciones teóricas, debido a que reduce drásticamente el número de átomos que pueden ser simulados en una computadora. La aplicación del método G-TDH permite reducir el costo computacional y estudiar las propiedades del estado básico como función del tamaño del cluster sin despreciar los efectos cuánticos. El método se basa en la construcción de una función de onda aproximada para el sistema, que consiste en un producto de Hartree de paquetes de onda uniparticulares con forma gaussiana. Estas funciones gaussianas se caracterizan por sus anchos y por sus centroides en los espacios de las coordenadas y de los momentos. Utilizando el principio variacional de Dirac-Frenkel-McLachlan y la técnica de propagación en tiempo imaginario, se obtienen las ecuaciones de movimiento que describen cómo estos parámetros se aproximan a los valores que describen el estado básico del sistema. Estos permiten obtener la función de onda del sistema y calcular las propiedades estructurales y energéticas del cluster en el estado básico.

PACS: Atomic and molecular clusters, 36.40.-c; Stability and fragmentation of clusters, 36.40.Qv; Structure of clusters, 61.46.Bc; Semiclassical methods, 31.15.xg

I. INTRODUCTION

The theoretical description of many-body quantum dynamics is a challenging task, and a key ingredient for the interpretation of experimental data on the dynamics of polyatomic molecules and condensed phase systems. Rare gas solids constitute model systems in which we can study the influence of quantum effects on the energetics and the structure of many-particle molecular systems as a function of the mass of the constituents. When dealing with lighter species, such as liquid helium or hydrogen, fully quantum-mechanical treatments (e.g., Path Integral Monte Carlo or wavepacket propagation techniques) are needed to account for the physical properties. In this case, the structural properties of the ground state can be computed via the relaxation method, involving imaginary-time propagation [1,2]. Due to the elevated computational cost associated with purely quantum dynamical methods, the number of atoms that can be simulated explicitly is rather small.

The Dirac-Frenkel-McLachlan variational principle [3, 4] often provides a suitable alternative to account for quantum effects on the nuclear motion. In this method, the time dependence of the wavefunction is mapped into the time-evolution of a set of parameters. Although imaginary-time-propagation of unconstrained state vectors approaches the ground state wavefunction for sufficiently long times for arbitrary initial conditions, a dependence of the computed ground state on the initial wavefunction is introduced via the wavefunction *ansatz*, since the propagation explores a reduced region of the Hilbert space.

The purpose of this work is the application of a highly efficient method to explore the energetics and the structure of the ground state of neon clusters of varying size, with emphasis on the assessment of the dependence of these properties on the initial conditions.

To this aim, we apply The Gaussian Time-Dependent Hartree (G-TDH) approach [4, 5]. Within this method, the many-particle wavefunction is written as a Hartree product of single-particle Gaussian wave-packets with time-dependent widths in position and momentum spaces. The application of the variational principle yields equations of motion for the wavefunction parameters, which are subsequently propagated in imaginary-time for neon clusters composed by up to 70 atoms. Although the G-TDH methodology has been used extensively to model the dynamics of polyatomic systems [6–9], a detailed analysis of the sensitivity of the results of this scheme on the initial conditions (i.e., the initial distribution of Gaussian wavepackets and their widths) is still lacking.

The paper is organized as follows. In section Methodology, the theoretical methods applied in this work are reviewed, including the Dirac-Frenkel-McLachlan variational method and the imaginary-time propagation. The computed structural and energetics properties, for neon clusters of varying size, are presented and discussed in section Results. The main conclusions and perspectives of this work are presented in the last section.

II. METHODOLOGY

II.1. *Hamiltonian of the system*

In the following, we consider a cluster composed by N neon atoms. The Hamiltonian of this system takes the form:

$$H = -\sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}_i} + U(\mathbf{R})\,, \tag{1}$$

where m is the mass of neon atoms, while $\mathbf{R} = \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N$ denotes the complete set of atomic positions. $U(\mathbf{R})$ is the total potential energy of the system, which is written as a superposition of Lennard-Jones pairwise interactions:

$$V_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{2}$$

The values of the energy ($\varepsilon = 1.34135\cdot 10^{-4}$ E$_h$) and length ($\sigma = 5.20242$ a$_0$) parameters of the interatomic potential energy curve (2) where taken from the literature [10].

Following Refs. [5] and [11], in order to obtain analytical expressions for the mean-field potentials and forces along each degree of freedom and to gain numerical efficiency, the Lennard-Jones potential is approximated as the sum of three Gaussian functions:

$$V_{LJ}(r) \approx \sum_{p=1}^{3} g_p e^{-b_p r^2}\,, \tag{3}$$

where $\{g_p\} = \{1849,\ -1.48,\ -23.2\}\cdot\varepsilon$, and $\{b_p\} = \{6.65,\ 0.79,\ 2.6\}\cdot\sigma^{-2}$. Although this approximate form will deviate from the original potential $V_{LJ}(r)$ for small interatomic separations, short-range repulsion forces prevent particles to get close enough for these differences to become noticeable.

II.2. *Imaginary time dependent Schrödinger equation and the Dirac-Frenkel-McLachlan variational method*

We are particularly interested in the properties of the quantum-mechanical ground state of the system. To compute the total wavefunction of the lowest energy state, an initial wavefunction $\Psi(\mathbf{R},0)$ is propagated according to the imaginary-time dependent Schrödinger equation (hereafter, atomic units are used):

$$-\frac{\partial}{\partial\tau}\Psi(\mathbf{R},\tau) = \hat{H}\Psi(\mathbf{R},\tau)\,. \tag{4}$$

The latter is obtained upon the substitution $t \rightarrow -i\tau$ in the Schrödinger equation. The imaginary-time dependent wavefunction $\Psi(\mathbf{R},\tau)$ approaches the N-particle ground state in the limit $\tau\rightarrow\infty$ (up to a normalization constant). This approach to the ground state of quantum mechanical system is known as the relaxation method [1,2].

In this work, equation (4) is solved by applying the Dirac-Frenkel-McLachlan variational principle

$$\left\langle \delta\Psi \middle| \frac{\partial\Psi}{\partial\tau} + \hat{H}'\Psi \right\rangle = 0 \tag{5}$$

to a suitable wavefunction *ansatz* $\Psi(\mathbf{R};\mathbf{z}(\tau))$, depending on the set of parameters $\mathbf{z} = (z_1, z_2, ..., z_n)$. In equation (5), $\hat{H}'$ stands for the Hamiltonian of the system in the center-of-mass reference frame.

Inserting the wavefunction $\Psi(\mathbf{R};\mathbf{z}(\tau))$ in expression (5) yields a set of equations of motion for the parameters.

II.3. *Gaussian Time-Dependent Hartree Method*

To obtain the parameters that describe the variational ground state of the system, an explicit form for the many-body wavefunction $\Psi(\mathbf{R};\mathbf{z}(\tau))$ is needed. Within the Gaussian Time-Dependent Hartree (G-TDH) method, the state vector is written as a Hartree product of normalized single-particle wavefunctions of Gaussian shape:

$$\Psi\Big(\mathbf{R},\mathbf{z}(\tau)\Big) = a(\tau)\prod_{i=1}^{N}\left(\frac{2\alpha_i(\tau)}{\pi}\right)^{3/4}\times \exp\Big[-\gamma_i(\tau)\Big(\mathbf{r}_i-\mathbf{r}_0^{(i)}(\tau)\Big)^2 + i\mathbf{p}_0^{(i)}(\tau)\Big(\mathbf{r}_i-\mathbf{r}_0^{(i)}(\tau)\Big)\Big]. \tag{6}$$

The wavefunction (6) depends on imaginary-time via the set of $3N+1$ parameters: the overall phase $a(\tau)$, the centers $\mathbf{r}_0^{(i)}(\tau)$ and $\mathbf{p}_0^{(i)}(\tau)$ of the ith-single-particle wavepacket in position and momentum spaces, respectively, and the width parameter $\gamma_i(\tau) = \alpha_i(\tau) + i\beta_i(\tau)$. The application of the variational principle (5) yields the following system of coupled first-order differential equations for the parameters

[5]:

$$\begin{aligned}
\dot{\mathbf{r}}_0^{(i)} &= \frac{\beta_i}{m\alpha_i}\left(\mathbf{p}_0^{(i)} - \frac{\mathbf{P}}{N}\right) - \frac{1}{2\alpha_i}\nabla_{\mathbf{r}_0^{(i)}} V\,, \\
\dot{\mathbf{p}}_0^{(i)} &= -2\frac{|\gamma_i|^2}{m\alpha_i}\left(\mathbf{p}_0^{(i)} - \frac{\mathbf{P}}{N}\right) - \frac{\beta_i}{\alpha_i}\nabla_{\mathbf{r}_0^{(i)}} V\,, \\
\dot{\alpha}_i &= -2\frac{\left(\alpha_i^2 - \beta_i^2\right)}{m}\left(1 - \frac{1}{N}\right) - \frac{8}{3}\alpha_i^2 V^{(\alpha_i)}\,, \\
\dot{\beta}_i &= -4\frac{\alpha_i\beta_i}{m}\left(1 - \frac{1}{N}\right)\,,
\end{aligned} \tag{7}$$

where $\mathbf{P}$ is the total linear momentum of the cluster.

The centroids $\mathbf{r}_0^{(i)}(\tau)$ and $\mathbf{p}_0^{(i)}(\tau)$ obey classical-like equations of motions on the effective multidimensional potential energy surface $V = \langle\Psi|U(\mathbf{R})|\Psi\rangle$, while the parameters α_i and β_i bring quantum delocalization effects into the formulation. Analytical expressions for the mean-field potential V and its derivatives $V^{(\alpha_i)} = \left\langle\frac{\partial\Psi}{\partial\alpha_i}|U(\mathbf{R})|\Psi\right\rangle$ in terms of the wavefunction parameters can be found elsewhere [12].

Once the parameters that define the shape of the many-body wavefunction $\Psi_0 = \Psi(\mathbf{R}, \tau \to \infty)$ have been computed, the centroids of the single-particle wavepackets $\mathbf{r}_0^{(i)}(\tau \to \infty)$ indicate the geometry of the cluster in its ground state. Likewise, the energy of the ground state can be calculated as the expectation value of the Hamiltonian in this limit:

$$E_0 = \left\langle\Psi_0\left|U(\vec{r_1}, \vec{r_2}, ..., \vec{r_N})\right|\Psi_0\right\rangle = \sum_{(s,t)}\sum_{p=1}^{3} g_p {A_{stp}}^{\frac{3}{2}} e^{-A_{stp}b_p {R_{st}}^2}\,, \tag{8}$$

where

$$A_{stp} = \frac{2\alpha_s\alpha_t}{2\alpha_s\alpha_t + b_p(\alpha_s + \alpha_t)} \text{ and } {R_{st}}^2 = \left({\vec{r_0}}^{(s)} - {\vec{r_0}}^{(t)}\right)^2 .$$

The integration of the system of equations (7) has a much lower computational cost compared to the numerical solution of the original time-dependent Schrödinger equation, thereby allowing to investigate the structural properties of much larger systems, although the search for the ground state is restricted to the region of Hilbert space spanned by the wavefunction *ansatz*.

III. RESULTS

In this section, we discuss the main results obtained by applying the G-TDH method to investigate the ground state structure of neon clusters. Specifically, we show how the initial conditions affect the energy of the optimized cluster structures obtained via imaginary-time propagation. Since the amount of local minima in the potential energy surface grows exponentially as the number of atoms increases, the initial conditions (from which the system of equations (7) is propagated) play an important roll in finding the global minimum, i.e., the asymptotically stable values of the parameters may correspond to the system being trapped in a local minimum.

In Figure (1), we show the ground state energies obtained for clusters with a number of atoms ranging from 2 to 70, using as initial condition the atoms placed in a b.c.c. crystal structure. Circles represent the results of calculations starting with narrow Gaussians ($\lambda = 0.15\ d_{min}$), whereas squares represent the values computed starting with broad Gaussians ($\lambda = 0.30\ d_{min}$), where d_{min} represents the nearest neighbor separation in the corresponding lattice and $\lambda = \frac{1}{\sqrt{4\alpha}}$ stands for the width of the gaussian wavepackets.

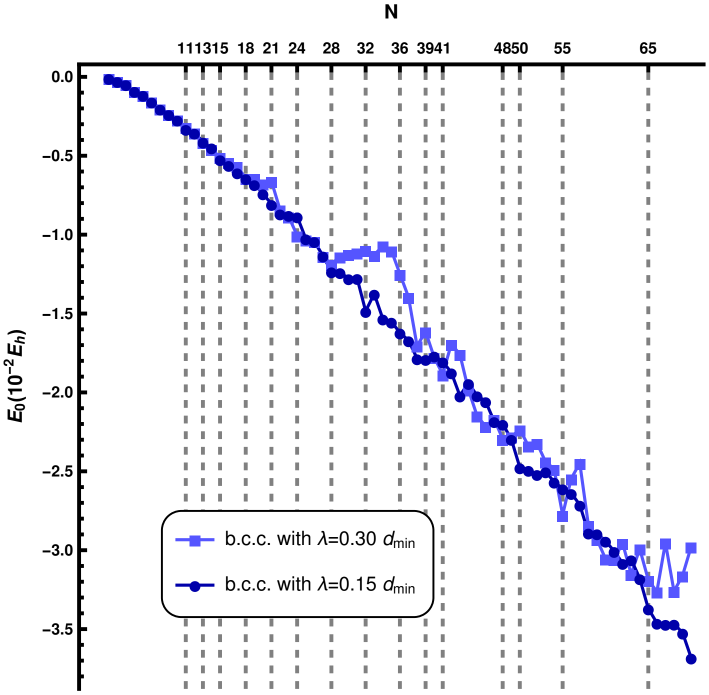

Figure 1. Ground state energy E_0 of neon clusters as a function of the number of atoms in the aggregate using a b.c.c. crystal structure as initial condition.

In Figure (2), we plot the dependence on the cluster size of the total energy of the aggregates. Their optimized structures were generated propagating equations of motion in imaginary-time and starting from different lattice structures, namely the simple cubic (s.c.), body-centered cubic (b.c.c.) and face-centered cubic (f.c.c.) lattices. Rare gas systems crystallize in the f.c.c. structure, so this configuration is expected to dominate the ground state geometry of clusters in the thermodynamic limit. However, it can be seen that other distributions may constitute more suitable starting points to find the ground state of the smaller clusters.

The sensitivity of the G-TDH to the initial placement of the atoms shown in Figure (2), points to the necessity to perform several simulations starting from different configuration arrangements, in order to obtain a reliable description of the ground state of the system. This increases the computational cost of the overall procedure. Nevertheless, since the imaginary-time evolution is local in the parameter space, the computational cost scales linearly with the number of atoms. Therefore, the present methodology continues to be advantageous for the investigation of large clusters, with respect to the direct solution of the multidimensional

Schrödinger equation (for the later, the effort required increases exponentially with the system size).

It can be noticed, that the initial localization of the particles have a non-negligible effect on the computed ground state energy. As expected, initial conditions have a more pronounced influence on the optimized geometry of larger clusters because of the increasing amount of local minima on the potential energy surface. This effect is more pronounced in the b.c.c. case. Interestingly, the initial placement of the atoms has only a mild influence on the energy of asymptotic structures obtained using s.c. and f.c.c. crystal sites as initial condition for the parameters $\vec{r}_0^{(i)}$.

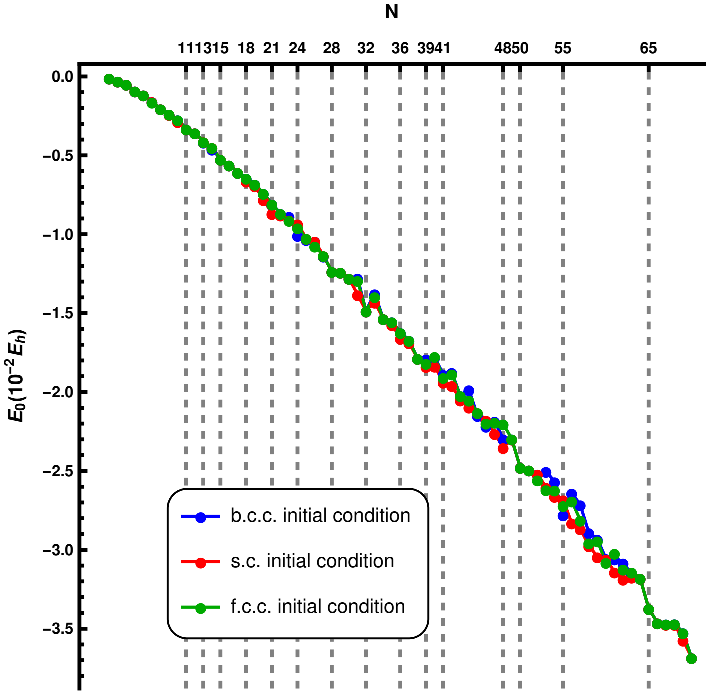

Figure 2. Ground state energy E_0 of neon clusters as a function of the number of atoms in the aggregate using a b.c.c., s.c. and f.c.c. crystal structures as initial conditions.

In both figures, the vertical dashed lines indicate magic numbers, i.e, the sizes of the clusters which are more stable than the closest ones ($E_0(N) < E_0(N-1)$ and $E_0(N) < E_0(N+1)$). The enhanced stability is associated with the completion of a solvation shell in the process of formation of the cluster by the sequential addition of individual atoms. For the magic number aggregates, the average number of nearest neighbors is maximized, thereby decreasing the total potential energy. These magic numbers can be identified as local minima in a E_0/N *vs.* N plot. To this purpose, we picked the configuration with the lowest energy for each cluster size, irrespective of the initial condition used to generate it.

In the literature, it is well established that clusters formed by N =13, 55, 147, ... rare gas atoms (which correspond to the completion of highly symmetrical icosahedral structures) constitute magic numbers, while there is considerable dispersion in the values of the magic numbers reported for other cluster sizes (which depend on the details of the interaction potential and the methodology used to generate the optimized structures) [11]. The capability to reproduce the magic numbers with the aforementioned number of atoms constitute a standard test of the optimization method employed in the investigation of the minimum energy structures of rare gas clusters, and it contributes to validate the G-TDH approach used in this work to characterize the geometries and the energetics of neon clusters.

IV. CONCLUSIONS

The G-TDH method was applied to the study of the ground state of neon clusters. This method markedly reduces the computational effort required to simulate these clusters, and it makes possible the study of aggregates with a large number of atoms without neglecting quantum effects. It allows to analyze the properties of the cluster as a function of the number of atoms, eventually bridging the gap between the gas and the condensed phases. The results of the simulations show that the optimized structures generated via imaginary-time propagation depend sensitively on the initial conditions chosen for the wavefunction parameters. Such dependence arise from the competition between the non-local character of the effective potential $\langle \Psi | U(\mathbf{R}) | \Psi \rangle$ on which the system evolves in the $\mathbf{r}_0^{(i)}, \mathbf{p}_0^{(i)}$ phase-space (which allows it to hop between the basins corresponding to different local minima, as it is verified for some of the examples presented in the Results section) and the down-hill motion in the direction of the local gradient at the point $\mathbf{r}_0^{(1)}, \mathbf{r}_0^{(2)}, ..., \mathbf{r}_0^{(N)}$. Therefore, the use of the G-TDH approach to investigate the ground state properties of neon clusters, requires equations (7) to be propagated starting from different initial conditions, in order to maximize the probability to find the global energy minimum.

REFERENCES

[1] P. Bader, S. Blanes, and F. Casas, J. Chem. Phys. 139, 124117 (2013).
[2] R. Kosloff, Chem. Phys. Lett. 127, 223 (1986).
[3] P. Kramer and M. Saraceno, *Geometry of the Time-Dependent Variational Principle in Quantum Mechanics*, (Springer Lecture Notes in Physics, 1981).
[4] S. Rau, J. Main, and G. Wunner, Phys. Rev. A 82, 023610 (2010).
[5] W. Unn-Toc, L. Uranga Piña, C. Meier, N. Halberstadt, and J. Rubayo Soneira, J. Chem. Phys. 137, 054112 (2012).
[6] E. J. Heller, J. Chem. Phys. 62, 1544 (1975).
[7] H. Cartarius and E. Pollak, J. Chem. Phys. 134, 044107 (2011).
[8] P. Elliott and N. T. Maitra, J. Chem. Phys. 135, 104110 (2011).
[9] J. Ono and K. Ando., J. Chem. Phys. 137, 174503 (2012).
[10] L. Uranga Piña, A. Martínez Mesa, J. Rubayo Soneira and G. Rojas Lorenzo, Chem. Phys. Lett. 429, 450 (2006).
[11] P. A. Frantsuzov and V. A. Mandelshtam, J. Chem. Phys. 128, 094304 (2008).
[12] W. Unn-Toc, Dynamique quantique de systèmes atomiques et moléculaires dans des agrégats de gaz rares (l'Université Toulouse, 2012).