PHYSICAL REVIEW B VOLUME 60, NUMBER 3 15 JULY 1999-I

Approximate density matrices for spherical metal clusters

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(Received 27 May 1998; revised manuscript received 3 February 1999)

On the sole basis of the knowledge of the expectation values of several physical observables, an inferred density matrix for spherical alkali-metal clusters is obtained. No explicit knowledge of any Hamiltonian model is assumed. A combination of information theory with the pseudoinverse variational formalism is employed, and densities for spherical Na clusters are obtained. [S0163-1829(99)09127-4]

I. INTRODUCTION

During the last years, several theoretical models have been applied in order to understand both static and dynamic properties of alkali-metal clusters measured in the pioneering experiments of Knight *et al.*[1,2] For small clusters ''*ab initio*'' calculations are available,[3] while in the case of large ones approaches based on the energy density-functional formalism (EDF) have provided a reasonable description of some experimental physical observables.[4,5]

The simplest model based on the EDF assumes that the main properties of these alkali-metal clusters can be described by the quantized motion of the valence electrons in a mean field generated by (i) their mutual interaction as described by the EDF and (ii) the attraction of a positive ionic background, modeled as a uniformly charged ''jellium'' sphere (JM). In such a scenario, the theoretical plasmon resonance has a blueshift with respect to the experimental values.[6,7]

Recently, more elaborated models have been applied. Reference is to be made, for instance, to the pseudopotential jellium model (PPJM) that accounts for the ionic structure. Here the electron-ion interaction is given by the Bachelet, Hamann, and Schlüter realistic nonlocal pseudopotential.[8] This model is able to greatly diminish previous discrepancies between theory and experiment, for optical spectra and polarizabilities, that plagued the conventional jellium model.[9]

One would like to be in a position to infer a wave function for our systems from available experimental information. It is our goal here that of exploring such a possibility by advancing a Hamiltonian-independent information theory (IT)-based way of obtaining an approximate density matrix for clusters.

As an application, we will show that it is clearly able to discriminate between the PPJM approach and the jellium model for describing metal clusters. More precisely, we shall in the present effort examine, for the case of spherical alkali-metal clusters, the predictions of our information theory-based approach that, without explicit use of any Hamiltonian, yields a model-independent density matrix from the sole knowledge of the expectation values (EV) of a few physical observables. These EV will be extracted from the PPJM and jellium models. It will be seen that the IT approach is able to closely reproduce each of the model's density matrices.

For the purpose of building up our model-independent density matrix, we have used M physical observables of r and k spaces and we have inferred, with the help of the pseudoinverse variational formalism,[10–12] the ground-state density matrix in a space of dimension N ($M<N$). In this process the unknown observables that we need for the complete determination of the density matrix are considered as variational parameters. The formalism is applied to Na clusters with closed shells, using as input information the expectation values of some operators obtained with the different models one wishes to compare. The paper is organized as follows: In Sec. II, we provide a brief reminder of the EDF within both the jellium and the pseudojellium strictures. The pseudoinverse formalism is presented in Sec. III. Results are presented in Sec. IV, and some conclusions are drawn in Sec. V.

II. EDF FORMALISM

In the EDF formalism we assume that the total energy E of a cluster with $\overline{N}$ valence electrons is given by

$$E=E_{kin}+E_{xc}+E_{es}+E_{ei}\,, \tag{1}$$

where E_{kin} is the kinetic energy of a noninteracting electrons, while E_{xc}, E_{es}, and E_{ei} refer to the exchange-correlation, the electrostatic, and the electron-ion parts of the total energy, respectively.

The electrostatic repulsion direct term is

$$E_{es}=\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{2}$$

where $\rho(\mathbf{r})$ is the diagonal density of valence electrons. The exchange-correlation term is taken in the local-density approximation (LDA) with the parametrization of Ref. 13. The electron-ion term in the JM becomes

$$E_{ei}=\int d\mathbf{r}\rho(\mathbf{r})v_j\,, \tag{3}$$

where v_j is the potential produced by an uniformly charged sphere.

In the case of the PPJM the electron-ion energy is

$$E_{ei}=\sum_{i(occ)}\int d\mathbf{r}\phi_i^*(\mathbf{r})v_{ps}\phi_i(\mathbf{r}), \tag{4}$$

where v_{ps} is an external nonlocal potential of $\overline{N}$ ions, given by the spatial average of the ion electron interaction inside the jellium sphere,[9] and the sum is over the occupied states with single particle wave function $\phi_i(\mathbf{r})$.

The minimization of the total energy gives us the Kohn-Sham model equations that, in the PPJM, adopt the form

$$\left\{-\frac{1}{2}\nabla^2+\int d(\mathbf{r})\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+V_{xc}[\rho(\mathbf{r})]+v_{ps}\right\}\phi_i(\mathbf{r})$$

$$=\epsilon_i\phi_i(\mathbf{r}), \tag{5}$$

where $V_{xc}[\rho(\mathbf{r})]=\delta E_{xc}/\delta\rho(\mathbf{r})$. Note that v_{ps} is replaced by v_j in the jellium ansatz. The self-consistent solution of the Kohn-Sham radial equations yields the single-particle wave function ϕ_i and the single-particle eigenenergies ϵ_i. Notice that, in the PPJM, nonlocal effects produce an effective orbital-dependent potential, contrary to what happens in the case of the jellium model, where the mean field is the same for all valence electrons. With the single-particle wave functions a density matrix is obtained for both models, and, consequently, the expectation values of relevant observables obtained in the usual fashion

$$d_r=\langle\hat{A}_r\rangle=\text{Trace}\ \ (\hat{\rho}\hat{A}_r). \tag{6}$$

These expectation values, computed within the framework of the PPJM or JM models, will be taken as the input information of our IT-based pseudoinverse variational formalism.

III. INFORMATION THEORY BASED PSEUDOINVERSE FORMALISM

The central idea of the present formalism is that of inferring, by recourse to information theoretic tools, an approximate density matrix. To this end, the pertinent prior knowledge is assumed to be that of M expectation values that correspond to a set of noncommuting operators $\hat{A}_r(r=1,\ldots,M)$.

In order to actually implement this methodology[10–12] a Hilbert space basis (in principle, arbitrary) $\{|i\rangle\}$ must be appropriately selected. In practical calculations one always deals with a finite subspace of dimension, for example, N. Consequently, our density matrix is an $N\times N$ matrix, which entails that $N^2\equiv\mathcal{N}$ pieces of information must be inferred out of M pieces of data. The concomitant inference process can thus be viewed as a mapping

$$\mathcal{R}^M\rightarrow\mathcal{R}^{\mathcal{N}}. \tag{7}$$

In these spaces, the density matrix can be viewed as an N^2-dimensional vector $\vec{f}\in\mathcal{R}^{\mathcal{N}}$ and the input information as an M-dimensional one $\vec{d}\in\mathcal{R}^M$.

Notice that if the density matrix were to be known, those expectation values that comprise our data would arise from a mapping inverse to the one above

$$\mathcal{R}^{\mathcal{N}}\rightarrow\mathcal{R}^M, \tag{8}$$

effected by a rank deficient operator $\hat{G}$ that maps vectors from $\mathcal{R}^{\mathcal{N}}$ into vectors belonging to $\mathcal{R}^M$. This operator $\hat{G}$ is represented in our chosen basis by an $M\times N^2$ matrix whose elements are, in turn, the matrix elements of the operators $\hat{A}_r$, i.e., one orders the pairs $i=1,\ldots,N;\quad j=1,\ldots,N$ in some, for example lexicographic order so as to assign to each pair an appropriate index $l(i,j),\quad(l=1,\ldots,N^2)$, and writes

$$\mathbf{G}_{r,l(i,j)}=\langle i|\hat{A}_r|j\rangle;\quad r=1,\ldots,M;\quad l=1,\ldots,N^2. \tag{9}$$

With these notational conventions it is clear that our informational *a priori* knowledge can be cast into the form

$$\vec{d}=\mathbf{G}\vec{f}, \tag{10}$$

which can be viewed as a *direct* linear problem (if one knows $\vec{f}$, compute the M expectation values that define $\vec{d}$). But the crux of the matter is that we need to solve the associated *inverse* problem, as exemplified by Eq. (7). It is shown in Refs. 10–12 that a maximum entropy approach (MEP) to the task yields a convenient solution in terms of the Moore-Penrose pseudoinverse[14] operator $\hat{P}_{MP}$, whose matrix representation reads

$$[\hat{P}_{MP}]\equiv\mathbf{P}_G=\mathbf{G}^{tr}(\mathbf{G}\mathbf{G}^{tr})^{-1}, \tag{11}$$

where the supraindex above indicates matrix transposition. The MEP approximate density matrix is then given by

$$\vec{f}_{MEP}=\mathbf{G}^{tr}(\mathbf{G}\mathbf{G}^{tr})^{-1}\vec{d}, \tag{12}$$

which neatly expresses our inferred density matrix in terms of the input data $\vec{d}$ and the known matrix $\mathbf{G}$. For more details and illustrative applications the reader is referred to Refs. 10–12.

IV. RESULTS

The formalism reviewed in the preceding section has been applied to the inference of ground-state density matrices in the case of some spherical metal clusters. It is assumed that each single-particle wave function $\phi(\mathbf{r})$ can be suitably expanded in a harmonic oscillator basis

$$\phi_{nlm}(\mathbf{r})=\sum_{n'=1}^{K}C_{n'l}R_{n'l}(r)Y_{lm}(\Omega), \tag{13}$$

where the $C_{n'l}$ are unknown overlap coefficients to be determined according to the information theoretic tools described above, and the $R_{n'l}(r)$ refer to harmonic oscillator (HO) ra-

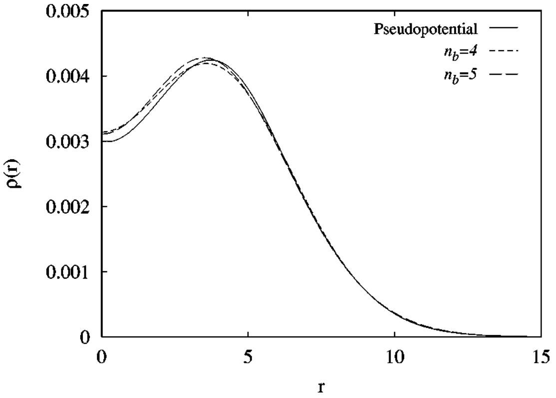

FIG. 1. PPJM ground-state electronic density of Na_8 obtained by recourse to different basis sizes for the same input information consisting of $\langle r^2\rangle$, $\langle p^2\rangle$, $\langle r^4\rangle$, and $\langle r^6\rangle$.

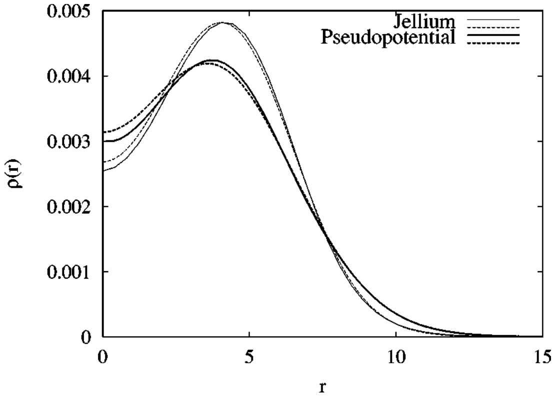

FIG. 2. Kohn-Sham electronic densities for Na_8 clusters predicted by the jellium model (thin line) and by the pseudopotential jellium model (thick line). Exact model results (solid lines) are compared to those inferred with the present approach (dashed lines).

dial wave functions. For simplicity, we have chosen the HO radial basis because (i) it is of an analytical character and (ii) it depends only on one parameter that can be obtained from the input information $\langle r^2\rangle$.

It is obvious that if the above expansion includes enough terms our results will be basis independent. This condition can be verified by comparing the results obtained from two distinct expansions that differ only in their respective numbers of terms. Thus, in order to study the influence of the expansion size in our results we compare in Fig. 1 the PPJM ground-state electronic density of Na_8 obtained using (i) a basis with five orbitals $(n_b=5)$ and (ii) a basis with four orbitals $(n_b=4)$. Of course, the input information is the same in both cases (for more details see caption of Fig. 1). Notice that the result for $n_b=4$ is very close to the one corresponding $n_b=5$. For $n_b=3$ (this instance is not depicted) the basis is too small and the concomitant results not satisfactory. The ensuing practical recipe would be to include as many expansion terms as needed to ensure that the results are quasiindependent of the expansion-size.

In general, in order to infer n_s single-particle states (13) by recourse to a basis expansion in terms of $K=n_b$ orbitals, $n^2=(n_b n_s)^2$ expectation values (of independent observables) are required. However, since we are going to be dealing with real, symmetric density matrices ρ, just $\mathcal{N}=[n(n+1)]/2$ become actually necessary.

Notice also that our systems are characterized by spherical symmetry, so that each single-particle state is characterized by the angular quantum number l. The orthogonality of the spherical harmonics allows for a further reduction of $\mathcal{N}$, as $n_b^2[n_s(n_s-1)]/2$ overlap coefficients will vanish identically. As a consequence, the number of independent observables whose expectation values we need turns out to be

$$\mathcal{N}=n_s\frac{n_b(n_b+1)}{2}. \tag{14}$$

Our input information will consist of $M<\mathcal{N}$ expectation values of noncommuting observables. Let us call $D=\mathcal{N}-M$.

In practical computations a caveat of our formalism must be kept in mind.[12] The IT-method is not provided with the information that the diagonal elements of the density matrix ρ must be of a positive-definite character. Neither does it ''know'' that we are to infer a pure state, whose thermodynamical entropy

$$S_{thermo}=-\mathrm{Trace}[\rho\ \ln(\rho)] \tag{15}$$

is zero.

As shown in Ref. 12, these facts can be gainfully employed in a ''variational-like'' fashion. We select D-independent observables and consider their expectation values as parameters entering our calculation. The idea is to repeatedly apply the pseudoinverse formalism for different values of these parameters so as to ensure both a positive-definite ρ and $S_{thermo}=0$. In order to accomplish this goal we define a cost function,

$$J=\sum_{i=1}^{n}|w_i||\ln(|w_i|)|+|w_i|, \tag{16}$$

where w_i are the eigenvalues of the density matrix. The cost function J is always positive and corresponds to the pure state when its value is equal to n_s, as we have then only one $w_i=1$ for each single-particle state. This value is also the

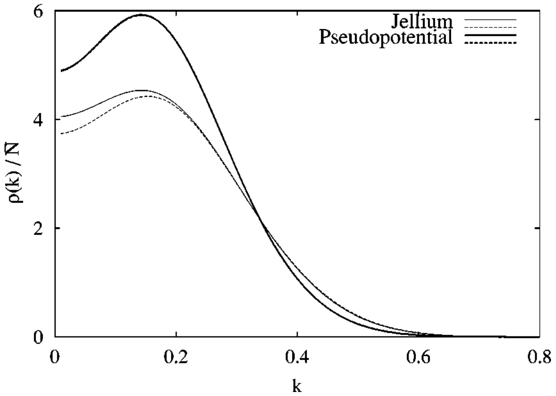

FIG. 3. Kohn-Sham electronic momentum densities per atom for Na_8, as predicted by the jellium model (thin lines) and the pseudopotential jellium model (thick lines). Exact model results (solid lines) are compared to those inferred with the present approach (dashed lines).

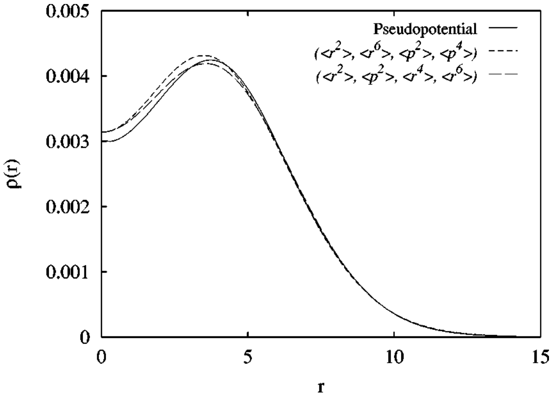

FIG. 4. PPJM ground-state electronic density of Na_8 obtained by recourse to different sets of input information for the same basis.

minimum one it can adopt. Thus, our problem is translated into a minimization problem with D variables. Unfortunately, this is not a convex problem so that local minimization algorithms are not adequate. We have used, instead, the method of simulated annealing[15] to find a pure state compatible with our information. The precision of the result can be improved afterwards by recourse to a local minimization technique, in our case the downhill simplex method.[16]

Figures 2 and 3 display, for the case of Na_8, the ground-state electronic density and the momentum distribution inferred from the input information consisting of

$$\langle r^2\rangle, \quad \langle p^2\rangle, \quad \langle r^4\rangle, \quad \langle r^6\rangle \tag{17}$$

together with the number of particles of each shell. These expectation values are calculated according to the tenets of the models we wish to compare.

In order to test the influence of the input operators, we depict in Fig. 4 the PPJM ground-state electronic density of Na_8 obtained from two different sets of ‘‘input’’ operators: the one referred to above and that obtained when we change $\langle r^4\rangle$ by $\langle p^4\rangle$. Both densities closely resemble each other. In the general case, the concomitant results may obviously depend upon the input information, but in practice a working recipe could be that of choosing low moments of $\rho(r)$ and $e(k)$. We can speculate that the most suitable experimental information will be provided by these expectation values obtained, as in the nuclear physics case, from elastic e scattering and from the momentum distribution of the valence electrons obtained with electron knock-out experiments.[17]

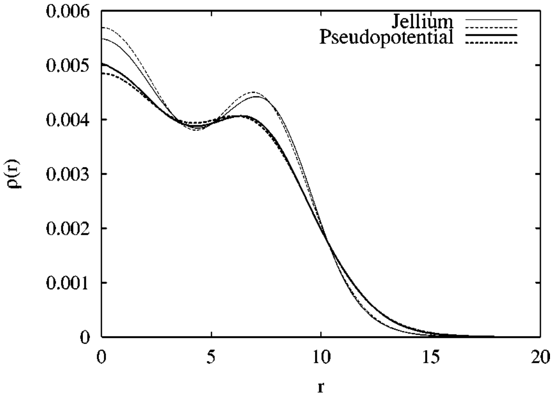

FIG. 5. Same as Fig. 2 but for the Na_{20}.

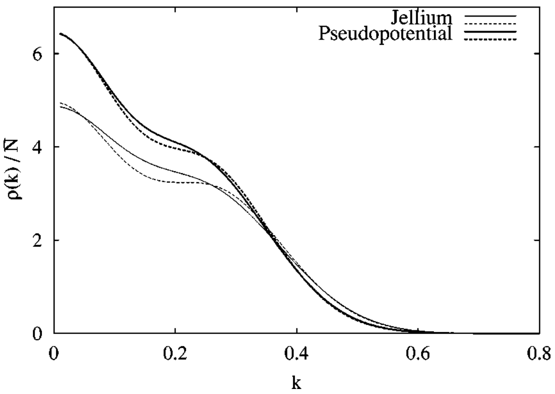

FIG. 6. Same as Fig. 3 but for the Na_{20}.

The HO parameter of the $R_{nl}(r)$ wave functions is determined, for each shell, from the value of $\langle r^2\rangle$. A truncated basis of four oscillators $n_b=4$ proves to be sufficient for the task at hand (see Fig. 1). Since for Na_8 one has $n_s=2$, our working variational space is a 10-dimensional one.

For the Na_{20} a truncated basis of five oscillators $n_b=5$ is required. In this case, one has $n_s=4$, and thus a 36-dimensional variational space. The input information used is the same as in Eq. (17) with the addition of $\langle 1/r\rangle$. Our inferred results are compared to the exact ones in Figs. 5 and 6, both for r and k spaces. The degree of agreement is indeed remarkable.

Notice that from the profiles shown in Figs. 2, 3, 5, and 6, it becomes clear that our formalism nitidly discriminates between the two models considered in the present effort. In addition, starting from the coefficients of our inferred density matrix our formalism provides single-particle wave functions of rather good quality (they closely resemble those of the concomitant models) for both EDF models, as illustrated by Figs. 7 and 8.

Notice that our inferred wave functions are obtained with the help of a few data and *without* recourse to the Kohn-Sham self-consistent procedure.

V. CONCLUSIONS

We have developed a variational pseudoinverse formalism that allows us to infer, in a rather satisfactory fashion,

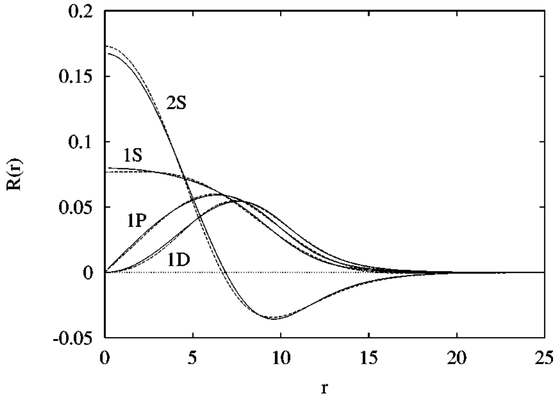

FIG. 7. Kohn-Sham Na_{20} single-particle wave functions obtained with the jellium model (solid lines) are compared to those inferred with the present approach (dashed lines).

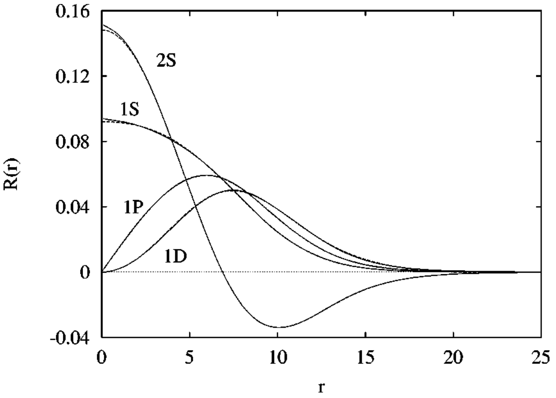

FIG. 8. Same as Fig. 7 but for the pseudopotential jellium model.

the density matrix of spherical alkali-metal clusters. The validity of our approach has been checked with reference to the jellium model and the PPJM one. We have calculated a few expectation values from these models, given them as informational input to our algorithm, and shown that the model's density matrix is satisfactorily reproduced.

Our input information is restricted to M expectation values, corresponding to noncommuting observables. We do not assume any knowledge concerning the system's Hamiltonian. Our results are, consequently, of a model-independent character. We have shown, that with the help of a few data, a quite reliable (in the sense that it resembles closely the model's one) cluster wave function can be constructed. The corresponding results are of a remarkably good quality, both for r and k spaces.

We conjecture then that, if similar kinds of information were experimentally obtained, the *actual* cluster density matrix could be inferred in the same fashion.

ACKNOWLEDGMENTS

This work has been performed under the auspices of the General Agreement signed between the Universities of Illes Balears and Nacional de La Plata, the Spain–Spanish-America Scientific Cooperation Program AECI (1998), and the DGICYT-PB95-0492-A grant (Spain).

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