Full configuration-interaction study of the metal-insulator transition in model systems

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Abstract. The precursor of the Metal-Insulator transition is studied at ab-initio level in equally-spaced Liₙ and Beₙ linear chains. In particular, large-size Full Configuration-Interaction (FCI) calculations (up to one billion determinants for Li₈ and half a billion for Be₅) have been performed. At FCI level, it is possible to take into account the different nature of the electronic wavefunction at the different internuclear distances. Several indicators of the Metal-Insulator transition (minimum of the Koopmans energy gap, maximum of the localization and polarizability tensors) are considered and discussed. It is shown that the three considered properties indicate a Metal-Insulator transition at distances that are in remarkable agreement.

1. Introduction
The transition from a metallic to an insulating behavior is a fundamental subject in solid-state physics. The transition can be classified according to the interaction responsible of the insulating behavior (for a detailed discussion of the different types of transitions, see, for instance, reference [1]). In particular, a Metal-Insulator (MI) transition can occur when the interatomic distance of a metallic system is sufficiently increased, so that the electrons become localized on different atoms. This type of phase transition is often called a Mott transition, after the works of N.F. Mott (see reference [2]).

Although, strictly speaking, it is possible to talk of a MI phase transition only in infinite systems, some of the elements that characterize this type of transition are already present in systems of moderate size. In the following of this paper, terms like “metal”, “insulator”, and “MI transition” will be used, in this restricted sense, for finite systems. The advantage of dealing with finite systems is that they can be accurately described by using sophisticated Quantum-Mechanical methods. It is possible, in this way, to understand a phenomenon at a microscopic level.

The MI transition in a model system composed of ten lithium atoms disposed on a ring had been studied by one of us by using Multi-Reference Configuration Interaction (MRCI) approaches [3, 4]. More recently, we performed Full Configuration Interaction (FCI) calculations on linear lithium clusters [5]. In the present contribution, FCI results on linear lithium and beryllium...
chains with respect to a MI transition are presented and discussed. We notice that a FCI approach, thanks to its total flexibility, is particularly suited to describe wavefunctions having different characters. In fact, FCI permits to follow, in a continuous way, a changing-nature wavefunction, from the short-bond metallic to the long-bond insulating regions.

In the present contribution, we present FCI calculations obtained on linear lithium and beryllium chains. Four lithium chains (Li$_n$, $n = 2, 4, 6, 8$) and four beryllium chains (Be$_n$, $n = 2, 3, 4, 5$) have been considered. The largest FCI calculations involve about one billion (for Li$_8$) and half a billion (for Be$_5$) symmetry-adapted Slater determinants, and are close to the limits of present-day FCI capabilities. Odd values of $n$ have been discarded in the case of lithium, since they correspond to an open-shell ground state for the neutral system. Since beryllium has an even number of electrons, the problem is not present for this species. Linear chains, with respect to cyclic rings, have the clear drawback of showing border effects. They present, however, a few distinct computational advantages, particularly if the system is treated at a FCI level. Linear chains have a high $D_{x<h}$ symmetry, (that is reduced to the abelian $D_{2h}$ in our actual FCI calculations), which considerably reduce the computational cost: in fact, only the $n = 6$ cyclic case would be feasible with present-day FCI technology. Moreover, closed-shell ground states for the neutral lithium rings follow the “$n = 4m + 2$” rule of aromatic systems [6]. Finally, small rings have bond angles significantly different from linearity, and the extrapolation of the different values of $n$ would be problematic.

Different criteria can be used to distinguish a metallic phase from an insulating one. This is discussed in the theory of the insulating state [8], and its extensions [9]-[12]. We notice that, although this formalism has been developed in the framework of Periodic Boundary Conditions, its extension in the case of finite non-periodic clusters [13] is clearly more appropriate for the present investigation.

As discussed by Resta in reference [13], it can be shown that these, apparently different, criteria are in fact equivalent. For an infinite system, they are:

(i) Zero energy gap for the low-lying electronic excitations.
(ii) Infinite per-atom polarizability.
(iii) Infinite fluctuation of the position operator.

As any other phase transition, a genuine MI transition can be observed only in infinite systems. In a finite cluster, however, it is possible to find a behaviour that indicates the trend toward the infinite-system regime. In the present work, these quantities are computed, for the different chains, as a function of the internuclear distance, and their behaviors are compared. All these indicators undergo a rapid change at an internuclear distance (about 7 bohr for lithium and 5 bohr for beryllium) that depend only weakly on the chain length. Moreover, this behavior becomes more pronounced as far as the size of the system is increased. These results can be interpreted as the indication of a MI phase transition, in the infinite system, at about this internuclear distance.

2. Criteria for Metallic or Insulating Behavior

Three equivalent criteria can be considered in order to characterize a MI transition. It should be stressed that these are necessary but not sufficient criteria, as pointed out in reference [1]. In this section, these criteria that are briefly presented and discussed. A more complete treatment can be found in reference [5]

2.1. The Energy Gap.

The (exact) energy gap, $\Delta$, is defined as the difference between the Ionization Potential (IP) and the Electron Affinity (EA) of the system (see, for instance, reference [14]):

$$\Delta = \text{IP} - \text{EA}$$  \hspace{1cm} (1)
In the case of a purely monoelectronic Hamiltonian, the ground-state total energy is given by the sum of the occupied spinorbital energies,

\[ E(n) = \sum_{i=1}^{n} \epsilon_i \quad (2) \]

On the other hand, the ionic ground states having \( n - 1 \) and \( n + 1 \) electrons have energies:

\[ E(n - 1) = \sum_{i=1}^{n-1} \epsilon_i = E(n) - \varepsilon_{\text{HOMO}} \quad (3) \]

and

\[ E(n + 1) = \sum_{i=1}^{n+1} \epsilon_i = E(n) + \varepsilon_{\text{LUMO}} \quad (4) \]

respectively. Here \( \varepsilon_{\text{HOMO}} \) and \( \varepsilon_{\text{LUMO}} \) are the energies of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). Therefore, in this case, the exact gap \( \Delta \) is equal to the one-electron energy gap, \( \delta \), defined as

\[ \delta \equiv \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}} \quad (5) \]

For this reason, the one-electron gap \( \delta \) often called the HOMO-LUMO gap.

In the case of a two-electron Hamiltonian, like the electron Hamiltonian used in \textit{ab initio} calculations, the gap \( \Delta \) can be computed via equation (1). It is also possible, however, to define one-electron energies obtained from the correlated wavefunction through the formalism of the Extended Koopmans Theorem (EKT) \cite{15}-\cite{20}. In this formalism, the total Hamiltonian of the system is diagonalized in the (non orthogonal) basis sets \{\( a_i | \Psi_0 > \)\} and \{\( a^+_j | \Psi_0 > \)\}, where \( | \Psi_0 > \) is the ground-state eigenvector and the \( a_i \) and \( a^+_j \) are the usual second-quantization annihilation and creation operators. In this way, variational upper bounds for the singly charged cationic and anionic systems, respectively, are obtained. By subtracting the energy of the neutral system, one-electron energies can be defined, which are associated to the correlated wavefunction. Therefore, it is possible to \textit{approximate} the gap \( \Delta \) via an equation which is formally identical to eq. (5). From a computational point of view, eq. (5) is more convenient than eq. (1) since a single FCI calculation is required (instead of three) in order to obtain the gap. Moreover, for a filling less than one half, the FCI treatment of negative ions is much more heavy than the neutral system. Finally, we notice that, in the limits of validity of the Extended Koopmans Theorem, \( \delta \) tends to \( \Delta \) for a complete basis set. For a finite basis, as discussed in reference \cite{5}, the two gaps give essentially the same indications as far as the MI transition is concerned. For these reasons, all the correlated energy gaps presented in this work have been computed from the FCI wavefunction through the EKT formalism. Notice that, if the SCF wavefunction is used instead of the FCI one, the SCF orbital energies are obtained.

\subsection{2.2. The Localization Tensor}

We follow the definition of the Localization Tensor given by Resta \cite{13}. If we indicate by \( \hat{r}_i \) the position operator of the \( i \)-th electron, the total position for the whole system is the one-electron operator given by:

\[ \hat{r} = \sum_{i=1}^{n} \hat{r}_i \quad (6) \]

It has three cartesian components \( \hat{r}_\beta \) (\( \beta = x, y, z \)).
Given any electronic wavefunction $|\Psi\rangle$ and an operator $\hat{O}$, one defines the momenta of order $k$ by $<\hat{O}^k> = <\Psi|\hat{O}^k|\Psi>$. In our case the momenta have tensorial nature and we can compute the matrix elements: $<r_\beta r_\gamma \ldots> = <\Psi|\hat{r}_\beta \hat{r}_\gamma \ldots|\Psi>$. It is also possible to perform a cumulant expansion of these momenta [13]. The cumulant of the quadratic fluctuation of the position is defined as [13]:

$$<r_\beta r_\gamma> = \frac{1}{n} (<\Psi|\hat{r}_\beta \hat{r}_\gamma|\Psi> - <\Psi|\hat{r}_\beta|\Psi><\Psi|\hat{r}_\gamma|\Psi>)$$

(7)

Notice that the $\frac{1}{n}$ factor has been introduced to have a quantity that, for $n$ identical non-interacting systems, does not depend on $n$. In the following, for the sake of simplicity of notation, the localization tensor $<r_\beta r_\gamma>_c$ will be simply indicated as $\rho_{\beta\gamma}$.

The localization tensor can also be expressed in the spectral-resolution form as:

$$<r_\beta r_\gamma>_c = <\Psi_0|r_\beta - r_\beta>(r_\gamma - r_\gamma)\Psi_0 = \sum_{k>\Psi_0} <\Psi_0|r_\beta|k><k|r_\gamma|\Psi_0>$$

(8)

### 2.3. The Electron Polarizability

The linear response of the system to an external oscillating electric field is determined by the complex polarizability tensor [28]. The usual electric polarizability is the real part of the complex tensor and it can be expressed in the spectral form:

$$\alpha_{\beta\gamma}(\omega) = \sum_{k>0} \left( \frac{<\Psi_0|r_\beta|\Psi_k><\Psi_k|r_\gamma|\Psi_0>}{E_k - E_0 - \omega} + \frac{<\Psi_0|r_\beta|\Psi_k><\Psi_k|r_\gamma|\Psi_0>}{E_k - E_0 + \omega} \right)$$

(9)

where $|\Psi_k>\,$ are the eigenvectors of the system, in ascending order of energy $k = 0, 1, 2, \ldots$, while $|\Psi_0>\,$ and $E_0$ are the ground-state wavefunction and energy respectively.

In the following of this paper, we will always make use of the polarizability divided by the number of atoms, $n$. The similarities between the localization and the polarizability tensors are emphasized when they are expressed in the spectral-resolution form: they are both properties of the state $|\Psi_0>\,$ of the system, although the other states enter into its definition via the sum over the excited states.
3. Results and Discussion

We used the gaussian ANO basis set optimized by Widmark et al. [21]. In particular, the 3s1p contraction was selected in this work for both lithium and beryllium. This basis set is a very small one, consisting of only six Atomic Orbitals (AO) for each lithium or beryllium atoms. For this reason, the present results must be considered essentially qualitative, especially as far as second order properties (i.e., polarizabilities) are concerned. However, the reduced size of the basis set enabled us to perform FCI calculations up to the Li$_8$ and Be$_5$ chains, that would have been absolutely untreatable by using larger basis sets. The overall qualitatively behavior of the involved quantities is nonetheless correctly reproduced even with this small basis set.

The SCF calculations have been done by using the DALTON ab initio package [22], that was also used to produce the file containing the AO one- and two-electron integrals. The integrals were subsequently transformed on the Molecular Orbital (MO) basis set, via the Ferrara four-index transformation [23]. All the FCI calculations (total energy, Koopmans energies, localization tensor, polarizabilities, entropies) have been performed by using the Bologna FCI code [24],[25], interfaced to the DALTON and the Ferrara transformation code via the Q5Cost library [26, 27]. In all the FCI computation, the 1s electrons have been frozen at the SCF level. This makes a basis set of five MO’s per lithium atom for the FCI calculations.

The energy curves of the Li$_n$ and Be$_n$ systems are illustrated in Figures 1 and 2, respectively. In order to make the comparison between the different values of $n$, the energies per atom are plotted. In the case of lithium, there is a minimum between 5.0 and 6.0 bohr, whose depth and position do not depend strongly on the number of atoms. For beryllium, on the other hand, the smallest clusters do not have any minimum at all, and this is due certainly to the smallness of the basis set [29]. The largest systems, on the other hand, show a shallow minimum between 4.0 and 4.5 bohr.

In Figures 3 and 4, the HOMO and the LUMO EKT energies computed from the FCI wavefunction are shown. Notice that, in the distance range we have investigated, there are no changes in the symmetry of the frontier orbitals (either SCF or FCI), and the HOMO and LUMO energies are smooth functions of the internuclear distance $R$.

In Figure 5, the Koopmans’ gaps for the SCF and FCI wavefunctions are reported for the case of Li$_n$. The SCF gaps show no minimum, and the long-distance behavior is very different from the FCI case. In fact, in this case, the SCF wavefunction has an incorrect “metallic” dissociation limit. The FCI values of the gap, on the other hand, converge towards the free-atom limit. The
**Figure 5.** \( \text{Li}_n \) chains: SCF (KT) and FCI (EKT) gaps as a function of the inter-atomic distance.

**Figure 6.** \( \text{Be}_n \) chains: FCI (EKT) gaps as a function of the inter-atomic distance.

**Figure 7.** \( \text{Li}_n \) chains: parallel and perpendicular (per atom) polarizability tensor as a function of the inter-atomic distance.

**Figure 8.** \( \text{Li}_n \) chains: parallel and perpendicular (per atom) polarizability tensor as a function of the inter-atomic distance.

**Figure 9.** \( \text{Li}_n \) chains: parallel and perpendicular localization tensor as a function of the inter-atomic distance.

**Figure 10.** \( \text{Be}_n \) chains: parallel and perpendicular localization tensor as a function of the inter-atomic distance.
Be₉ chains, illustrated in Figure 6, show a more concordant behavior between SCF and FCI, due to the dominant presence of the SCF determinant in the FCI wavefunction.

In Figures 7 and 8, the polarizabilities per atom computed at the FCI level, are reported. The behavior of the perpendicular polarizability, \( \alpha_\perp \), show a very weak dependence from \( n \), with the tendency to a slight growth as the size of the system is increased. As a function of the interatomic distance, \( \alpha_\perp \) increases as \( R \) increases, and tends monotonically to the isolated atomic value for large values of \( R \). The parallel polarizabilities, \( \alpha_\parallel \), on the other hand, have a completely different behavior. Short values of \( R \) show parallel polarizabilities numerically similar to the perpendicular ones. When \( R \) is increased, \( \alpha_\parallel \) has a steep rising, up to a maximum located at about 7.0 bohr lor Li and 5.0 for Be. The height of the maximum increases very quickly with increasing values of \( n \). For even larger values of \( R \), the parallel polarizabilities decrease, down to the constant value of an isolated atom at large distances, with a behavior similar to \( \alpha_\perp \).

The behavior of the localization tensor is shown in Figures 9 and 10, and is very similar to the trend shown by the polarizability. We plot the perpendicular and parallel components, \( \rho_\perp = \langle r_x r_x \rangle_c \) and \( \rho_\parallel = \langle r_z r_z \rangle_c \). It can be seen that the maximum of the parallel component grows slower than the polarizability as a function of \( n \).

For an infinite system, the correlated energy gap (either \( \delta_{\text{FCI}} \) or \( \Delta_{\text{FCI}} \)) is expected to be zero for values of \( R \) that are shorter than the MI transition distance. For larger distances, the gap grows until it reaches the isolated-atom value. Correspondingly, the parallel polarizability and parallel localization tensor show the opposite trend: they diverge before the MI transition distance, then they lower to reach the isolated-atom values. For finite systems, and in absence of a sharp MI transition, the excitation gap lowers as the distance \( R \) increases (see the uncorrelated HOMO-LUMO gap of the SCF wavefunction for the lithium systems). In a similar way, the polarizability and localization tensors increase as a function of \( R \) (see the perpendicular components).

Some important points should be remarked:

(i) For a fixed length of the chain, the positions of the gap minimum and the polarizability maximum coincide remarkably.

(ii) The MI transition distance shortens when the chain length becomes longer, and it converges to values independent from the chain length.

Finally, it is a remarkable fact that the “signature” of the MI transition can already be seen in the behavior of the dimer.

4. Conclusions

The different possible indicators of a MI transition (energy gap, localization tensor, electron polarizability) present remarkably concordant behaviors in the case of the studied systems. In particular, the localization tensor and the electron polarizability have emerged as powerful tools to locate the transition between the metallic and insulating states. An important practical difference exists between these two indicators, as far as the computational cost is concerned: the localization tensor, can be straightforwardly computed from the wavefunction. The polarizability, on the other hand, is considerably more expensive, since it requires an additional iterative procedure whose cost is comparable with the eigenvector calculation.

An important point that has emerged from the present study is that, for a fixed length of the chain, the positions of the gap minimum and the localization and polarizability maxima coincide remarkably. Moreover, the MI transition distance is not very sensitive to the system size, and it quickly converges to a value independent from the chain length.

In the future, we plan to study with the same approach other systems. It should be noticed that FCI results can give precious informations to assess the reliability of approximated,
and more practical, methods. In particular, it would be possible to apply Multi-Reference Configuration Interaction or Coupled Cluster approaches to deal with this type of systems. A further aspect that will be considered, and that was already addressed in reference [3], is the emergence of a Peierls instability. In particular, it will be interesting to compare the behavior of lithium and hydrogen model chains, both Peierls distorted and undistorted, with respect to the MI transition.

The investigation of three-dimensional systems will also be considered. Preliminary results on beryllium clusters, for instance, indicate that the long-distance, insulating behavior of this closed-shell system can be correctly described at Coupled-Cluster level, at least in the case of relatively small systems. If these results are confirmed, different and larger systems could be investigated.

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References
[1] Gebhard F 1997 The Mott Metal-insulator Transition: Models and Methods, (Springer)
[2] Mott N 1990 Metal-insulator Transitions, 2nd edition, (Taylor and Francis)
[3] Paulus B, Rosciszewski K, Fulde P, and Stoll H 2003 Phys. Rev. B 68, 235115
[4] Alsheimer W and Paulus B 2004 Eur. Phys. J. B 40, 243
[5] Vetere V, Monari A, Bendazzoli G L, Evangelisti S, and Paulus B 2008 J. Chem. Phys. 128, 024701
[6] See, for instance, Coulson C A 1961 Valence, 2nd edition, (Oxford: Oxford University Press)
[7] McLachlan A D and Ball M A 1964 Rev. Mod. Phys. 36, 844
[8] Kohn W 1964 Phys. Rev. A 133, 171
[9] Resta R 1998 Phys. Rev. Lett. 80, 1800
[10] Resta R and Sorella S 1999 Phys. Rev. Lett. 82, 370
[11] Souza I, Wilkens T, and Martin R M 2000 Phys. Rev. B 62, 1666
[12] Resta R 2005 Phys. Rev. Lett. 95, 196805
[13] Resta R 2006 J. Chem. Phys. 124, 104104
[14] Martin R M 2004 Electron Configuration: Basic Theory and Practical Methods, (Cambridge: Cambridge University Press)
[15] Koopmans T C 1934 Physica 1, 104
[16] Day O W, Smith D W, and Garrod C 1974 Int. J. Quantum Chem. Symp. 8, 501
[17] Smith D W and Day O 1975 J. Chem. Phys. 62, 113
[18] Morell M M, Parr R G, and Levy M 1975 J. Chem. Phys. 62, 549
[19] Ahrichs R 1976 J. Chem. Phys. 64, 2706
[20] Katrie L J and Davidson E R 1980 Proc. Natl. Acad. Sci. U.S.A. 77, 4403
[21] Widmark P-O, Malmqvist P- A, and Roos B O 1990 Theor. Chim. Acta 77, 291
[22] DALTON, a molecular electronic structure program, Release 2.0 (2005) see http://www.kjemi.uio.no/software/dalton/dalton.html
[23] Cimiraglia R and Angeli C, private communication.
[24] Bendazzoli G L and Evangelisti S 1993 J. Chem. Phys. 98, 3141
[25] Gagliardi L, Bendazzoli G L, Evangelisti S 1997 J. Comp. Chem. 18, 1329
[26] Angeli C, Bendazzoli G L, Borini S, Cimiraglia R, Emerson A, Evangelisti S, Maynau D, Monari A, Rossi E, Sanchez-Marin J, Salay P G, Tajti A 2007 Int. J. Quant. Chem. 107, 582
[27] Borini S, Monari A, Rossi E, Tajti A, Angeli C, Bendazzoli G L, Cimiraglia R, Emerson A, Evangelisti S, Maynau D, Sanchez-Marin J, and Salay P G 2007 J. Chem. Inf. Modell. 47(3), 1271
[28] Landau L D, Lifshitz EM and Pitaevskij LP 1980 Course of Theoretical Physics vol. 5, Statistical Physics part 1, 3rd Ed. (Oxford New York Toronto Sydney Paris Frankfurt: Pergamon Press)
[29] Evangelisti S, Bendazzoli G L and Gagliardi L 1994 Chem. Phys. 185, 47