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Constant electronic energy trajectories in abstract nuclear charge space and level set topology

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The boundaries defining the electronic energy level set topologies in abstract nuclear charge space $^N\mathbf{Z}$ of molecular systems are analyzed. Several rigorous properties are derived, from which new results on geometry-independent constraints of electronic energy hypersurfaces are obtained. The asymptotic behavior of the boundaries at atomic pairwise-infinite separation is approximated making use of density functional theory. The relationships obtained for such a boundary allow one to evaluate very simply (just with a pocket calculator) upper and lower bounds to the electronic energy which are of interest in the study of chemical reactions and conformations. The procedure is also applied to discuss the feasibility of certain molecular ionization processes, as well as to derive some inequalities concerning atomic ionization potentials.

I. INTRODUCTION

The abstract nuclear charge space $^N\mathbf{Z}$ (a vector space whose elements are vectors having as components the nuclear charges of the atoms in an N -atomic molecule) has been the subject of several studies in the literature.

For instance, the \mathbf{Z} -continuous representation of the electronic energy has been used to prove many rigorous properties related to several bounds and convexity relationships¹⁻⁷ of the energy functional, in particular in the context of the methods of level set topology.³⁻⁶ The approach provided by this topologization has proved to be very convenient to obtain simple global analyses of the electronic energy hypersurfaces for polyatomic systems.

As an example, it has been shown recently⁶ that, for a given reference value of energy, there exists a fixed region of the $^N\mathbf{Z}$ space in which the molecular electronic energy hypersurface always lies above that reference value, for all conformational geometries. Such a constraint is of value for applications of chemical interest, especially in quantum theory of reaction paths and molecular conformations, and as a potential aid in computer-based synthesis planning. However, the determination of such a region, although straightforward, requires numerical information about the electronic energy for some atoms,⁶ and consequently loses the appeal of the first, but less powerful, fully geometrical approach.⁵

The purpose of this paper is to present some new developments about the level set topologization of $^N\mathbf{Z}$, with the aim of recovering a fully geometrical approach to the geometry-independent constraints to the ground-state electronic energy. The key of our proposal is what we have called "constant-energy trajectories" (CET), i.e., functions in $^N\mathbf{Z}$ representing arrays of nuclei with different nuclear charges, with the restriction of having a constant value of the electronic energy for each molecular conformation. For simplicity, we

will keep the term "trajectories" even in the case of multidimensional functions.

The CET's are basically the level set boundaries defining the subsets in $^N\mathbf{Z}$ from which the topology is built.⁴⁻⁶ In this paper we demonstrate several analytical properties of these boundaries and especially those of their limit in the atomic pairwise-infinite-separation configuration. These last results, derived in the approximate framework of the density functional theory (DFT), are the ones which allow us to recover the fully geometrical approach mentioned above.

The organization of the paper is as follows: in Sec. II we discuss some rigorous properties of the CET's. Particular emphasis is given to curvature properties for a given geometry, and to their dependence upon isotropical and nonisotropical dilatations of the configuration. In Sec. III we analyze the properties of the CET associated with the infinite separation configuration (limit trajectory). Our model of CET leads naturally to the introduction of a continuous representation for the number of electrons, which allows us to use the DFT in order to deduce upper and lower bounds to the limit trajectory. In Sec. IV we give some examples of applications of the new bounds to diatomic molecules. Taking as illustrative examples the C and N isoelectronic series, we show that *a family of molecular energy surfaces can be bounded between two atomic energies* using simple geometric considerations. The limitations of the method in the case of low number of electrons are also discussed in this section. Some consequences for the atomic and diatomic molecule ionization potentials are included as well. In Sec. V we apply the results of Sec. III to triatomic molecules. Extensions of the method and further comments are found in Sec. VI.

II. CONSTANT ENERGY TRAJECTORIES IN NUCLEAR CHARGE SPACE

Let us consider a system of N nuclei or pseudonuclei (i.e., the extension to noninteger nuclear charge). The vector \mathbf{Z} identifies the nuclear charge vector whose i th compo-

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nent is the charge of the i th nucleus. Let w be the number of internal coordinates necessary to describe the geometry of such an arrangement; then $\mathbf{r} \in {}^w\mathbf{R}$ is a vector describing the (internal) nuclear configuration of the molecule. Eventually, the dimension w can be chosen so that the vector \mathbf{r} contains redundant coordinates without altering our discussion; for instance, \mathbf{r} can be chosen as the vector having as components those of the position vectors of the nuclei ($w = 3N$).

We shall assume that the nuclear configuration space ${}^w\mathbf{R}$ is provided with a metric and that one of the nuclei is fixed at the origin of the laboratory frame. In this case we may choose $w = 3N - 3$.

It is convenient to classify the geometries in ${}^w\mathbf{R}$ into an infinite number of families, each family generated by an isotropic dilatation from an element \mathbf{r}_0 in the following set G :

$$G = \{\mathbf{r}_0 \in {}^w\mathbf{R}: \|\mathbf{r}_0\| = 1\}. \quad (1)$$

That is, the generators \mathbf{r}_0 are "isotropically independent" and any other geometry can be derived from one of them by means of a real parameter a : $\mathbf{r}(a) = a\mathbf{r}_0$, with $\mathbf{r}_0 = \mathbf{r}(1)$. This characterization of the geometry by means of the vectors in G will simplify our next discussion of functions on ${}^N\mathbf{Z}$.

Let us notice that, for a given $\mathbf{r} \in {}^w\mathbf{R}$, there is one and only one pair (a, \mathbf{r}_0) from which it can be derived, except for two cases: the limit of united atoms and the limit of pairwise-infinite separation. It is clear that

$$\lim_{a \rightarrow 0} \mathbf{r}(a) = \mathbf{0} \quad \text{for all } \mathbf{r}_0 \in G, \quad (2)$$

i.e., all the configurations in G give rise to the same structure after an isotropic (uniform) dilatation towards the united atom limit.

On the other hand, we notice that the energy of pairwise-infinite separation can be reached by uniform dilatation from any generator $\mathbf{r}_0 \in D$, $D \subset G$, where D is the subset of G containing all those generator nuclear configurations that have no coincident nuclear positions in the laboratory frame. We will associate this limit of the energy for $a \rightarrow \infty$ with a formal limit geometry $\mathbf{r}(a)$ indicated as \mathbf{r}_∞ (i.e., a formal vector having all its components infinity). That is, all the generators lead to the same structure by an infinite uniform dilatation (as long as those situations with two or more nuclei with coincident position in the laboratory frame are disregarded). It should be noticed that, except for the two above-mentioned limits, the ${}^N\mathbf{Z}$ space does not necessarily have any rotational symmetry. That is, for a given geometry \mathbf{r} the "exchange" of different nuclei may produce a new structure. On the other hand, the limits $a \rightarrow 0$ and $a \rightarrow \infty$ represent the situations of higher symmetry of the system.

A level set in ${}^N\mathbf{Z}$ space is defined in terms of a collection of nuclear charge vectors for which, for a given geometry \mathbf{r} , the electronic energy is higher than or equal to a given reference value E_0 . That is, the set can be characterized by two parameters \mathbf{r} and E_0 , or by three parameters (\mathbf{r}_0, a, E_0) using the set G . Such a level set has a boundary, the latter being a function describing, by definition, arrays of N nuclear charges constrained to have a constant electronic energy value. Such boundaries are, consequently, CET's in the line of our previous discussion. Based on the analysis of such trajectories one may rather easily test whether a molecule, in any

conformation, belongs to a given level set, that is, whether its energy is bounded by the value E_0 . Due to the many applications that can be based on such a prediction, we will devote the remainder of this section to deducing the most important features characterizing a CET.

Our purpose is now to study some analytical properties of these CET's as functions on ${}^N\mathbf{Z}$. This can be done in a simpler way if we write the CET's as nuclear charges. Let us suppose that we know the first $N - 1$ (arbitrarily labeled) nuclear charges; then the N th charge is automatically fixed by the constraint of constant electronic energy value, and it can be considered as a function of $N - 1$ variables. It can be shown easily that this function is, indeed, single valued for each geometry \mathbf{r} .⁸ In what follows the charge Z_N will be considered as the one defining the CET:

$$Z_N = f_{\mathbf{r}_0}(\mathbf{z}, a); \quad \mathbf{z} = (z_1, z_2, \dots, z_{N-1}) \in {}^{N-1}\mathbf{Z}, \quad (3)$$

where it is clearly stated that the trajectory $f_{\mathbf{r}_0}(\mathbf{z}, a)$ is associated to the geometry $\mathbf{r} = a\mathbf{r}_0$. In order to keep the notation as simple as possible we have omitted all reference to the constant value E_0 defining the level set.

In the context of the Born–Oppenheimer approximation, the electronic Hamiltonian describing an n -electron N -atomic molecule of geometry \mathbf{r} (whose nuclear charge vector belongs to a CET) can be written as

$$H_e = H_e(\mathbf{Z}, \mathbf{r}) = T_e + V_{ee} - \sum_{s=1}^{N-1} Z_s Q_s - f_{\mathbf{r}_0}(\mathbf{z}, a) Q_N, \quad (4a)$$

$$Q_s = \sum_{i=1}^n \|\mathbf{R}_i - \mathbf{r}_s\|^{-1}, \quad (4b)$$

where \mathbf{R}_i stands for the position vector of the i th electron and \mathbf{r}_s for that of the s th nucleus. Atomic units are used throughout and the rest of the symbols in Eq. (4) have their usual meaning.

Using Eq. (4a), the condition for a vector belonging to a CET is of course:

$$\langle H_e \rangle = E_e(\mathbf{Z}, \mathbf{r}) = E_e\{[\mathbf{z}, f_{\mathbf{r}_0}(\mathbf{z}, a)], a\mathbf{r}_0\} = E_0, \quad (5)$$

where the expectation values are taken over the electronic coordinates. The reference value E_0 can always be taken, without any loss of generality, as the energy of an atom of the n -isoelectronic series having a nuclear charge Z_0 (in general noninteger). This means that a CET must cross the N Cartesian coordinate axes that span ${}^N\mathbf{Z}$ at the value $Z_s = Z_0$, for $s \leq N$.

By definition of a CET, the value of energy functional $E_e(\mathbf{Z}, \mathbf{r})$ is invariant to changes of the components of the vector \mathbf{z} , whenever Z_N is given by Eq. (4). This fact gives us a complementary property defining a CET:

$$\frac{\partial E_e}{\partial z_i} = \frac{\partial^2 E_e}{\partial z_i \partial z_j} = \frac{\partial^3 E_e}{\partial z_i \partial z_j \partial z_k} = \dots = 0, \quad 1 \leq i, j, k, \dots \leq N - 1, \quad (6a)$$

where in taking these partial derivatives we consider E_e to be a function of \mathbf{z} , $f_{\mathbf{r}_0}(\mathbf{z}, a)$, and the vector \mathbf{r} . According to the Hellmann–Feynman theorem (HFT) we know:

$$\frac{\partial E_e}{\partial z_i} = \left\langle \frac{\partial H_e}{\partial z_i} \right\rangle, \quad i \leq N - 1. \quad (6b)$$

In our case, the Hamiltonian contains two terms dependent on z_i [cf. Eq. (4a)]. In one of these terms the dependence is linear, while in the other it is, in general, nonlinear [through the function $f_{r_0}(\mathbf{z}, a)$]. Taking into account these results, Eqs. (6) lead to the first partial derivatives of the function $f_{r_0}(\mathbf{z}, a)$ defining the CET:

$$\frac{\partial f_{r_0}(\mathbf{z}, a)}{\partial z_i} = -\frac{\langle Q_i \rangle_{\mathbf{z}, \mathbf{r}}}{\langle Q_N \rangle_{\mathbf{z}, \mathbf{r}}} < 0, \quad i \leq N-1, \quad (7)$$

where $\langle \cdots \rangle_{\mathbf{z}, \mathbf{r}}$ stands for the electronic expectation value with both geometry and nuclear charge vector fixed. This result holds for all exact bound states and for their variational approximations.

The derivative Eq. (7) fulfills some asymptotic properties which are of importance in deducing the most relevant features of the function $f_{r_0}(\mathbf{z}, a)$:

(i) In the united-atom limit ($a \rightarrow 0$) it is obvious that

$$f_{r_0}(\mathbf{z}, 0) = Z_0 - \sum_{s=1}^{N-1} Z_s \quad \text{for all } \mathbf{r}_0 \in G. \quad (8)$$

Furthermore, when the geometry \mathbf{r} collapses to $\mathbf{0}$, there is no distinction among the N nuclear positions, hence $Q_i = Q_N$, so we get from Eq. (7):

$$\lim_{a \rightarrow 0} \frac{\partial f_{r_0}(\mathbf{z}, a)}{\partial z_i} = -1, \quad i \leq N-1. \quad (9)$$

From Eqs. (8) and (9) it is deduced that the united-atom limit of the level set boundary is a hyperplane, furthermore, the following holds:

$$E_e\{\mathbf{z}, f_{r_0}(\mathbf{z}, a)\} > E_0(Z_0), \quad (10)$$

as long as $f_{r_0}(\mathbf{z}, a) < f_{r_0}(\mathbf{z}, 0)$, for all generators $\mathbf{r}_0, \mathbf{r}'_0$ in G . This result was previously discussed in Refs. 5 and 6.

(ii) Let us consider the reduction of the molecule to an isolated atom but *keeping the geometry constant*, i.e., letting all nuclear charges but one tend to zero. Let us assume, for instance, $\mathbf{z} \rightarrow \mathbf{0}$. In this case, we shall use the notation \mathbf{Z}_0 for a vector that has all of its first $(N-1)$ elements equal to zero, and the N th element equal to the value Z_0 . Taking into consideration that the electronic density of the isolated atom tends asymptotically to zero, we found that $\langle Q_i \rangle_{\mathbf{z}, \mathbf{r}} \rightarrow 0$ if $a \rightarrow \infty$ ($i \neq N$). As result Eq. (9) is still valid for $\mathbf{z} \rightarrow \mathbf{0}$, we conclude from Eq. (7) that the derivative of f_{r_0} is bounded in the limit of an isolated atom as follows:

$$\begin{aligned} -1 &= \lim_{a \rightarrow 0} \lim_{\mathbf{z} \rightarrow \mathbf{0}} \frac{\partial f_{r_0}(\mathbf{z}, a)}{\partial z_i} \leq \lim_{\mathbf{z} \rightarrow \mathbf{0}} \frac{\partial f_{r_0}(\mathbf{z}, a)}{\partial z_i}, \\ &\leq \lim_{a \rightarrow \infty} \lim_{\mathbf{z} \rightarrow \mathbf{0}} \frac{\partial f_{r_0}(\mathbf{z}, a)}{\partial z_i} = 0, \quad \text{for all } \mathbf{r}_0 \in G. \end{aligned} \quad (11)$$

Equation (11) describes the curvature properties of the CET in the neighborhood of the Z_N axis, but a simple relabeling of the variables shows that the same result must hold for all axes. This means that, in the neighborhood of each axis, the tangent plane to the CET at the limit \mathbf{r}_∞ is orthogonal to the axis. Owing to this, and to the fact that Eq. (11) establishes the upper bound to all derivatives, we conclude that all CET's are enclosed by a hypercube whose sides have length Z_0 , a result proven earlier using a different approach (cf. Ref. 5).

To provide a tighter bound to the CET's we need a further result. The set of CET's is a set of infinitely many boundaries; each of which is related through a factor $a \in \mathbb{R}$ to a geometry generator \mathbf{r}_0 . That is, one and only one set of CET's is associated to a vector \mathbf{r}_0 . Let us compare now two such CET's corresponding to two constants a and a' . Furthermore, let us choose the N th axis so that $Z_N \geq Z_i$, $i \leq N-1$; this choice restricts the analysis to a fully representative subset of the CET, the remainder of which can be obtained by a simple exchange of coordinate axes in $^N\mathbf{Z}$. The following discussion is based on an assumption, reasonable on physical grounds, and that would be expected to hold, at least, for all ground electronic states (see Refs. 2 and others cited therein) of molecules with nonnegative overall charge: The electronic density about the atom with the largest nuclear charge is not expected to decrease (under an isotropic dilatation of the molecular geometry) by a greater amount than those about the nuclei with lower charges. That is to say, under the above choice for Z_N ($Z_N \geq Z_i$, $i \leq N-1$), we assume that if $\langle Q_N \rangle_{\mathbf{z}, \mathbf{r}} \geq \langle Q_i \rangle_{\mathbf{z}, \mathbf{r}}$, then

$$\begin{aligned} \langle Q_N \rangle_{\mathbf{z}, \mathbf{r}} &= \langle Q_N \rangle_{\mathbf{z}, \mathbf{r}'} + A, \\ \langle Q_i \rangle_{\mathbf{z}, \mathbf{r}} &= \langle Q_i \rangle_{\mathbf{z}, \mathbf{r}'} + B, \quad i \leq N, \quad A \leq B > 0, \end{aligned} \quad (12a)$$

with $\mathbf{r} = a\mathbf{r}_0, \mathbf{r}' = a'\mathbf{r}_0, a < a'$. The truth of this inequality for multielectronic ground states is a hypothesis which remains to be proven. (See also the end of Sec. III for a discussion of negatively charged molecules.) Inequality (12a) leads immediately to

$$\langle Q_i \rangle_{\mathbf{z}, \mathbf{r}} / \langle Q_N \rangle_{\mathbf{z}, \mathbf{r}} \geq \langle Q_i \rangle_{\mathbf{z}, \mathbf{r}'} / \langle Q_N \rangle_{\mathbf{z}, \mathbf{r}'}. \quad (12b)$$

The above assumption and Eq. (7) result in the following inequality:

$$\frac{\partial f_{r_0}(\mathbf{z}, a)}{\partial z_i} \leq \frac{\partial f_{r_0}(\mathbf{z}, a')}{\partial z_i}, \quad a' > a, \quad i \leq N-1, \quad \mathbf{r}_0 \in G. \quad (13)$$

The equality in Eq. (13) corresponds to the particular case of $Z_N = Z_i$, for all $i \leq N-1$.

According to our previous discussion, we know that $f_{r_0}(\mathbf{0}, a) = f_{r_0}(\mathbf{0}, a')$, for all a and a' . We also know, from the behavior of the derivatives at the above limit $\mathbf{z} = \mathbf{0}$, that in the immediate vicinity of $\mathbf{z} = \mathbf{0}$ the inequality $f_{r_0}(\mathbf{z}, a) \leq f_{r_0}(\mathbf{z}, a')$, for each pair $a' > a$, holds. The equality is only valid at $\mathbf{z} = \mathbf{0}$. We want to prove that the behavior is general, that is, $f_{r_0}(\mathbf{z}, a) < f_{r_0}(\mathbf{z}, a')$ for every $\mathbf{z} \neq \mathbf{0}$ and $Z_N > 0$. In other words, we want to prove that two CET's corresponding to two different geometries cannot cross. We shall do this by showing that if one allows that there is a crossing, this leads to contradiction with inequality (13). If, contrary to the statement, we assume that there are crossings, then there must be a first crossing nearest to the point $\mathbf{z} = \mathbf{0}, Z_N = Z_0$. We shall prove that there cannot exist a first crossing. Since the CET for a' must approach the assumed crossing from above the other CET, the components of its gradient at that point must be more negative than those of the CET for a . Consequently, for the corresponding derivatives the inequality: $\partial f_{r_0}(\mathbf{z}^*, a') / \partial z_i < \partial f_{r_0}(\mathbf{z}^*, a) / \partial z_i$, must hold for every $i = 1, 2, \dots, N-1$ at the assumed crossing at \mathbf{z}^* . The strict inequality in the above relation is in contradiction

with conclusion (13), hence *crossing* is impossible at point \mathbf{z}^* . All that is allowed is the case of equality of the derivatives that corresponds to a mere osculation of the two CET's. This in turn implies that there are infinitely many CET's (all those for values a'' : $a \leq a'' \leq a'$) which all osculate at this point. This special possibility can occur only if the equality holds in Eq. (13), that is, if $Z_i = Z_N$, $i = 1, 2, \dots, N-1$. However, even this special case of osculation appears unlikely, since it would imply a constant energy along a uniform dilatation. In conclusion, crossing is impossible and osculation is unlikely. We may write

$$f_{r_0}(\mathbf{z}, 0) \leq f_{r_0}(\mathbf{z}, a) < f_{r_0}(\mathbf{z}, a') \leq f_{r_0}(\mathbf{z}, \infty), \quad a' > a. \quad (14)$$

Result (14) can be formally condensed into the following proposition:

Proposition I: The CET's corresponding to an electronic ground state of a molecule with nonnegative overall charge form a set of functions bounded from below by the hyperplane (9) and from above by the curve corresponding to the limit of pairwise-infinite separation (limit trajectory). All the region of ${}^N\mathbf{Z}$ space between such bounds is filled completely by the CET's. If condition (12) holds, then those boundaries which are related by a uniform dilatation of the same geometry generator vector \mathbf{r}_0 in configuration space ${}^w\mathbf{R}$ do not cross each other and do not osculate.

The result condensed in proposition I holds for each $E_0(\mathbf{Z}_0)$ defining the level set. This implies that for a given energy value E_0 , and for a given generator \mathbf{r}_0 , there is, if any, only one CET passing through a point $\mathbf{Z} \in {}^N\mathbf{Z}$; that is, there is a one to one correspondence between the accessible electronic energy values and the molecular geometries \mathbf{r} derived from isotropic dilatation of a generator \mathbf{r}_0 , for a given vector \mathbf{Z} .

Two consequences arise from this result:

(i) *Under an isotropic dilatation from a generator \mathbf{r}_0 , the ground-state electronic energy is a monotonously increasing function bounded from above by the limit of pairwise-infinite separation.*

(ii) *Under a nonisotropic dilatation the ground-state electronic energy may be nonmonotonous, but the previous bound must still hold.* This last conclusion is based on the fact that if there were a maximum above the limit it could be always related to the pairwise infinite separation through an isotropic dilatation, which contradicts (i).

The above-mentioned bounds have been discussed in the literature, but rigorous results have only been given for one-electron molecules.^{2,9,10} Our analysis above is not rigorous because it is based on property (12) of the electronic density which, although physically reasonable, we have not proved from first principles. However, it is clear that the approach to the problem provided by the CET's formalism provides a different viewpoint which might be useful in generalizing the rigorous proof of Refs. 2 to many-electron molecules.

In what follows of this section we present an alternative proof, for all $a > 0$, that the boundaries are concave-from-below functions of the nuclear charges, for the particular case of the ground state. The technique used here also provides partial results that we shall utilize in a subsequent anal-

ysis. Our demonstration is inspired by the procedure usually followed to study the dependence of the electronic energy on the internuclear separation of diatomic molecules.¹¹⁻¹³ In our case the argument is modified to deal with the nuclear charges, and generalized to the case of polyatomic molecules.

Let us consider a change in the first $N-1$ charges of a vector \mathbf{Z}^0 that still leaves the new vector \mathbf{Z}' in the same CET. The Hamiltonian operator can be expanded as

$$H_e(\mathbf{Z}', \mathbf{r}) = H_e(\mathbf{Z}^0, \mathbf{r}) + (\mathbf{z}' - \mathbf{z}^0) \circ [\nabla H_e]_{\mathbf{z}=\mathbf{z}^0} + \dots, \quad (15a)$$

where higher order terms do not necessarily vanish even for Hamiltonians linear in \mathbf{Z} , since ∇ is the gradient in the subset ${}^{N-1}\mathbf{Z}$ and not in space ${}^N\mathbf{Z}$.

Without any loss of generality, it is convenient for our purposes to choose an isotropic distortion $\delta\mathbf{z} = \mathbf{z}' - \mathbf{z}^0$, i.e.,

$$H_e(\mathbf{Z}', \mathbf{r}) = H_e(\mathbf{Z}^0, \mathbf{r}) + g[\mathbf{z}^0 \nabla H_e]_{\mathbf{z}=\mathbf{z}^0} + \dots, \quad (15b)$$

$$g = \|\delta\mathbf{z}\|/\|\mathbf{z}\|.$$

The change in the nuclear charges introduces a change in the electronic energy and in the electronic wave function:

$$E_e^{(m)}(\mathbf{Z}', \mathbf{r}) = E_e^{(m)}(\mathbf{Z}^0, \mathbf{r}) + g[\mathbf{z}^0 \nabla E_e^{(m)}]_{\mathbf{z}=\mathbf{z}^0} + \dots, \quad (16a)$$

$$\Psi_e^{(m)}(\mathbf{Z}', \mathbf{r}) = \Psi_e^{(m)}(\mathbf{Z}^0, \mathbf{r}) + g[\mathbf{z}^0 \nabla \Psi_e^{(m)}]_{\mathbf{z}=\mathbf{z}^0} + \dots, \quad (16b)$$

where, as above, ∇ is the gradient in ${}^{N-1}\mathbf{Z}$ and m is the quantum number of the state under discussion. In what follows we will assume that this state is bound. The first-order correction in Eq. (16b) can then be evaluated easily with the HFT:

$$[\mathbf{z}^0 \nabla E_e^{(m)}]_{\mathbf{z}=\mathbf{z}^0} = \langle (\mathbf{z} \cdot \nabla H_e) \rangle_{\mathbf{Z}^0, \mathbf{r}}^{(m)}, \quad (17)$$

and it is zero along a CET. On the other hand, the first-order correction in Eq. (16b) can be obtained with the Rayleigh-Schrödinger perturbation theory. For nondegenerate $\Psi_e^{(m)}$, we get

$$\mathbf{z}^0 \nabla \Psi_e^{(m)} = \sum_{s \neq m} \Psi_e^{(s)} \mathbf{z}^0 \langle \Psi_e^{(s)} | \nabla H_e | \Psi_e^{(m)} \rangle / (E_e^{(s)} - E_e^{(m)}), \quad (18)$$

where, as usual, the summation symbol must be understood as including the extension to the continuum. It should be noticed that the higher order terms in Eq. (15b) will not alter the result for the first derivative of the wave function given by Eq. (18).

If we make use of the result

$$\mathbf{z}^0 \nabla (\mathbf{z}^0 \nabla B) = \mathbf{z}^0 A_B \mathbf{z} + \mathbf{z}^0 \nabla B, \quad (A_B)_{ij} = \frac{\partial^2 B}{\partial z_i \partial z_j}, \quad (19)$$

then differentiation of Eq. (17) will give us the following result for the second derivatives of the energy:

$$[\mathbf{z}^0 A_E(m) \mathbf{z}]_{\mathbf{z}=\mathbf{z}^0} = \langle \mathbf{z}^0 A_H \mathbf{z} \rangle_{\mathbf{Z}^0, \mathbf{r}}^{(m)} - 2P, \quad (20a)$$

where

$$P = \sum_{s \neq m} |\langle \Psi_e^{(s)} | \mathbf{z}^0 \nabla H_e | \Psi_e^{(m)} \rangle_{\mathbf{Z}^0, \mathbf{r}}|^2 / (E_e^{(s)} - E_e^{(m)}). \quad (20b)$$

Equations (6) imply that the left-hand side of Eq. (20a) is zero; then, from Eq. (4a) we deduce

$$[\mathbf{z} \circ A_{f_0} \mathbf{z}]_{\mathbf{z}=\mathbf{z}^0} = -2P / \langle Q_N \rangle_{\mathbf{z}^0, \mathbf{r}}. \quad (21)$$

Equations (20) and (21) are valid for all bound states. However, we can assign a definite sign to the function P only in the case of the ground state. Consequently, Eq. (21) implies that all CET's for a nondegenerate electronic ground state ($m = 0$) in the Born–Oppenheimer approximation must be concave from below. Equation (21) will be useful in providing an approximate representation of the limit trajectory $f_{r_0}(\mathbf{z}, \infty)$.

It is also worth mentioning that an argument, similar to that used in Ref. 12, shows that the condition (21) for the curvature holds not only for the exact ground state but also for all the variational approximations to it.

III. APPROXIMATE CALCULATION OF THE LIMIT TRAJECTORY

As it was seen in the previous section the CET's are bounded from above by the limit trajectory $f_{r_0}(\mathbf{z}, \infty)$. It would be useful to find approximate representations for such a function, because it would allow one to establish immediately that all the molecules satisfying $Z_N > f_{r_0}(\mathbf{z}, \infty)$ possess electronic energies below $E_0(Z_0)$ for all geometries.

Let us suppose for the moment that the reference energy E_0 is that of an atom of nuclear charge Z_0 and n electrons, i.e., $E_0 = E_0(Z_0, n)$. In the limit $a \rightarrow \infty$ the molecule under consideration becomes a set of N isolated atoms, and of course the electronic energy $E_e(\mathbf{Z}, \mathbf{r})$ can be obtained additively:

$$E_0(Z_0, n) = \sum_{s=1}^{N-1} E_0(Z_s, n_s) + E_0[f_{r_0}(\mathbf{z}, \infty), n_N], \quad (22)$$

where n_s is the number of electrons associated with the atom of nuclear charge Z_s . Two properties are satisfied by the nuclear charges and number of electrons (cf. Sec. II, proposition I)

$$Z_0 \leq \sum_{s=1}^{N-1} Z_s + f_{r_0}(\mathbf{z}, \infty), \quad (23a)$$

$$n = \sum_{s=1}^N n_s. \quad (23b)$$

The limit boundary represents a collection of atoms with charge vector \mathbf{Z} satisfying Eqs. (22) and (23a). In particular, the case $Z_s = 0$ if $1 \leq s \leq N-1$, $Z_N = Z_0$ is always accessible. Let us suppose now that for any Z_s value consistent with Eq. (23a) the number of electrons n_s for the s th atom is *always* the same. If this were a possible situation, when $Z_s = 0$ ($1 \leq s \leq N-1$) then we would get that $E_0(Z_0, n)$ should be equal to $E_0(Z_0, n_N < n)$ (plus $n - n_N$ electrons in the continuum), a contradiction. This very simple analysis is sufficient to show that n_s has to be a *variable* linked to Z_s in order to have a properly defined limit boundary. In the real world n_s would be a discontinuous function of the nuclear charges, for all values of the parameter a . However, a discontinuous representation would require a detailed knowledge of the critical nuclear charges for which an atom with n_s electrons can sustain at least one bound

state. Due to the fact that this constitutes a difficult problem, and not in general simply addressable, in the following we will treat n_s as a continuous variable.

The previous discussion reveals that the limit CET is a function whose properties can be described in terms of a continuous representation of both nuclear charges and number of electrons. Within such a representation $f_{r_0}(\mathbf{z}, \infty)$ is a fully unphysical function defined by Eqs. (22) and (23). Nonetheless, this unphysical function provides the bound over all CET's which contain as particular cases all the real physical situations of interest.

The idea of having an n -continuous representation is, of course, not new, and can be related to a continuous description of the quantum numbers or occupancy of a shell (see, for example, Refs. 14–17). Density functional theory provides the natural framework to deal with such a problem, and consequently we will make use of it to get a simple model approach to the limit boundary. To our purpose it is enough to use the properties of the Thomas–Fermi (TF) atoms and ions,¹⁸ a model which is known to give the exact leading term of the Hartree–Fock energy for large nuclear charge.^{19,20} In particular, we are interested in some properties of the TF energy as a continuous function of Z_0 and n .^{14–17,21–27}

As discussed above, n_s and Z_s must be linked to determine the limit boundary. In particular, we have $n_s \rightarrow 0$ when $Z_s \rightarrow 0$ in order to remove the aforementioned contradiction in the limit of an isolated atom. In order to build the simplest model for the function $f_{r_0}(\mathbf{z}, \infty)$, we will assume that n_s and Z_s^p are proportional, where p is in general an unknown exponent. Taking into account the limit conditions at $Z_s = 0$ and $Z_s = Z_0$, we get the simple relation:

$$n_s = n(Z_s/Z_0)^p. \quad (24)$$

It is easily seen that condition (23a) implies $p > 1$, because when all nuclei are equal we have $n_s = n/N$, but, according to the results in Sec. II (proposition I, for $a > 0$), $Z_s > Z_0/N$.

Using Eq. (23b) and taking each n_s in the form (24), one can rewrite the latter as

$$n_s = n \left\{ 1 - \sum_{i=1}^{s-1} (Z_i/Z_0)^p - \sum_{i=s+1}^N (Z_i/Z_0)^p \right\}, \quad (25)$$

then, rearrangement and substitution of Eq. (3) for Z_N leads us to

$$f_{r_0}(\mathbf{z}, \infty) = \left\{ Z_0^p - \sum_{s=1}^{N-1} Z_s^p \right\}^{1/p}, \quad p > 1. \quad (26)$$

It is evident that the function (26) fulfills all the properties found in Sec. II for the first and second derivatives of a CET in ${}^N\mathbf{Z}$, and then it seems to be a reasonable approximation to the actual limit boundary.

To make relation (26) useful we must obtain some information about the exponent p . This can be accomplished in several ways. First of all, we can obtain qualitative upper and lower bounds to Eq. (26) using the results known for the chemical potential in the TF limit of atoms.^{26,27}

When Z_s is large and $n_s < Z_s$ we know^{26,27}

$$E_0(Z_s, n_s) = -A Z_s^{7/3} + A' Z_s^{7/3} (1 - n_s/Z_s)^{7/3}, \\ A > 0, \quad A' > 0, \quad A > A', \quad (27)$$

where $A' = 0.047\,310\,072\,6\dots^{27}$ and $A = 0.768\,745\,124\,2\dots$ (in the TF approximation). If we now introduce Eq. (27) into Eq. (22), and for the sake of simplicity we restrict ourselves to the isoelectronic sequence of an “atom” Z_0 (i.e., $n = Z_0$), the result is

$$Z_0^{7/3} = \sum_{s=1}^N Z_s^{7/3} - (A'/A) \sum_{s=1}^N Z_s^{7/3} (1 - n_s/Z_s)^{7/3} < \sum_{s=1}^N Z_s^{7/3}. \quad (28)$$

Let us notice that the result (28) must stand independently of the relation that exists between n_s and Z_s , for $n_s \leq Z_s$ and for all s . Our model (24) provides a link between n_s and Z_s disallowing the extreme cases with $n_s \ll Z_s$; however, we expect Eq. (28) to be valid even for low n_s , provided that Z_s is also small. From Eq. (28) we obtain a lower bound to the limit trajectory:

$$f_{r_0}(\mathbf{z}, \infty) > \left\{ Z_0^{7/3} - \sum_{s=1}^{N-1} Z_s^{7/3} \right\}^{3/7} = L_{Z_0}(\mathbf{z}). \quad (29)$$

Comparing Eqs. (29) and (26), we can expect $p > 7/3$. It must be stressed that, though Eq. (27) is strictly valid in the TF limit, the approximation is known to be acceptable even for $Z_0 = 1$.¹⁷ We will show later on that the bound Eq. (29) is in fact useful for most molecules of interest.

We can derive easily an upper bound to the limit boundary from the fact that $(1 - n_s/Z_s) < 1$, and using the properties of the constants A and A' [Eq. (27)]. It is clear that [cf. Eq. (28)]

$$f_{r_0}(\mathbf{z}, \infty) < \left\{ c Z_0^{7/3} - \sum_{s=1}^{N-1} Z_s^{7/3} \right\}^{3/7} = U_{Z_0}(\mathbf{z}), \quad c = (1 - A'/A)^{-1} = 1.049\,659\,5\dots \quad (30)$$

Relations (29) and (30) are some of the most useful ones among those discussed in this paper. Both allow one to get tight bounds to the limit CET and then make an accurate description of the level set possible. With regard to the validity of the model we can expect that, for the nondegenerate ground state of all n -electron molecules with charge vector \mathbf{Z} , the electronic energy in the Born–Oppenheimer approximation has the following three properties:

- (i) $E_e(\mathbf{Z}, \mathbf{r})$ is lower than the energy of a neutral n -electron atom $E_0(Z_0, n)$ if $Z_N > U_{Z_0}(\mathbf{z})$ [Region (i)].
- (ii) If $Z_0 - \sum_{s=1}^{N-1} Z_s < Z_N < L_{Z_0}(\mathbf{z})$, then there exists a geometry $\mathbf{r}^* \in {}^w\mathbb{R}$ so that $E_e(\mathbf{Z}, \mathbf{r}^*) = E_0(Z_0, n)$ [region (ii)].
- (iii) If $L_{Z_0}(\mathbf{z}) < Z_N < U_{Z_0}(\mathbf{z})$, then it can be expected that if \mathbf{r}^* exists it will be very close to the limit of atomic pairwise-infinite separation. This condition can be considered as chemically inaccessible for most purposes [region (iii)].

The results (i)–(iii) represent a fully geometrical description of the numerical bounds discussed in Ref. 6 (extending those in Ref. 5).

It should be noticed that, in order to establish the upper and lower bounds to $f_{r_0}(\mathbf{z}, \infty)$ from Eq. (27), we have introduced the restriction $Z_0 = n$. This constraint can be removed as shown later, using an approximation.

Although $L_{Z_0}(\mathbf{z})$ is a function with similar characteris-

tics to Eq. (26), $U_{Z_0}(\mathbf{z})$ is not. In the latter case we have a function that crosses the Cartesian axes of ${}^N\mathbf{Z}$ for $Z > Z_0$. In order to have information about those molecules having atoms with nuclear charges similar to Z_0 it would be important to provide an upper bound having the structure of Eq. (26). In what follows we show how this can be accomplished, removing at the same time the aforesaid constraint on the number of electrons.

Density functional theory allows one to approximate the electronic energy of an atom through the well-known $1/Z_0$ series^{21–27}:

$$E_0(Z_0, n) = Z_0^2 \sum_{s=0}^{\infty} e^{(s)}(n) Z_0^{-s}, \quad (31a)$$

whose coefficients $e^{(s)}(n)$ depend on the number of electrons in a continuous way, approximately given by Refs. 14–17, and references quoted there.

$$e^{(s)}(n) \approx n^{s+1/3} \{ K_s + (K'_s e^{(0)}(n) + K''_s) n^{-1/3} \}, \quad s \geq 1,$$

$$e^{(0)}(n) \approx -\text{const } n^{1/3}. \quad (31b)$$

Equations (31) give rise to a superimposed $n^{-1/3}$ and Z_0^{-1} power series expansion for the energy, whose leading terms imply Eq. (27) for $Z_0 = n \gg 1$. A first approximation to the energy, retaining the larger terms ($n \leq Z_0$), can be given as

$$E_0(Z_0, n) \approx -\text{const } Z_0^2 n^{1/3}. \quad (32)$$

Although Eqs. (31) and (32) are supposed to be more useful in the limit of both n and Z_0 large, their range of validity is rather wide. Shakeshaft and Spruch¹⁶ have estimated the radius of convergence of the $n^{-1/3}$ power series expansion using different models of shell filling, and the former seems to be fairly large. Then it is not surprising to have results whose usefulness extends even to $n < 1$.

We can obtain an approximate representation to the limit boundary, when the restriction of $n = Z_0$ is removed using Eq. (32). Inserting the latter equation in all the atomic energies in Eq. (22), and invoking our model constraint (24), we get

$$f_{r_0}(\mathbf{z}, \infty) \approx \left\{ Z_0^{2+p/3} - \sum_{s=1}^{N-1} Z_s^{2+p/3} \right\}^{3/(p+6)}. \quad (33)$$

Comparing Eqs. (33) and (26), it is suggested that a reasonable approximation to the exponent p would be the solution of $p = 2 + p/3$, i.e., $p = 3$. Of course this is consistent with the previously discussed condition $p > 7/3$. It is difficult to establish *a priori* how accurate is the following approximation:

$$f_{r_0}(\mathbf{z}, \infty) \approx F_{Z_0}(\mathbf{z}) = \left\{ Z_0^3 - \sum_{s=1}^{N-1} Z_s^3 \right\}^{1/3}, \quad (34)$$

but this can be estimated comparing $F_{Z_0}(\mathbf{z})$ with $U_{Z_0}(\mathbf{z})$ where, of course, the former fulfills the required approximate asymptotic conditions expected for the limit boundary. Taking into account that

$$[1 - (Z_s/Z_0)^2]^{7/3} + (Z_s/Z_0)^{2/3} < 1, \quad (35)$$

is valid if Z_s/Z_0 falls within the interval

$\mathbf{I} = (0.693\ 513\ 628\ 899\dots, 1)$, we deduce [using $p = 3$ in Eq. (24)] that

$$\sum_{s=1}^N Z_s^{7/3} (1 - n_s/Z_s)^{7/3} \leq \sum_{s=1}^N Z_s^{7/3} - Z_0^{-2/3} \sum_{s=1}^N Z_s^3, \\ Z_s/Z_0 \in \mathbf{I} \quad \text{for all } s \leq N. \quad (36)$$

Finally, comparing Eq. (36) with Eq. (28) we get

$$F_{Z_0}(\mathbf{z}) > U_{Z_0}(\mathbf{z}), \quad \text{if } Z_s/Z_0 \in \mathbf{I} \quad \text{for all } s \leq N, \quad (37)$$

that shows that in certain subset of ${}^N\mathbf{Z}$, $F_{Z_0}(\mathbf{z})$ is an upper bound. In a particular case the range given by Eq. (37) can be extended, determining the zeroes of the algebraic equation $U_{Z_0}(Z_1) = F_{Z_0}(Z_1)$ ($N = 2$). As a result, $F_{Z_0}(Z_1)$ is an upper bound to the limit CET for a diatomic molecule if

$$0.338\ 87\dots < (Z_1/Z_0), \quad (Z_2/Z_0) < 0.986\ 86\dots \quad (38)$$

There is still a region near the Cartesian axes about which little is known and where only property (iii) can be applied. In the next section we will test the utility of the bounds in such a region for the particular case of diatomic molecules.

The last analysis, based on the $n^{-1/3}$ expansion of the electronic energy, suggests that the bounds L_{Z_0} , U_{Z_0} , and F_{Z_0} can still hold in the case of $n = Z_0$, and even for low values of n . Of course that behavior will hold if the ground state is a bound state in the subset of ${}^N\mathbf{Z}$ under consideration. This certainty excludes the molecular isoelectronic sequences derived from highly negative "atomic" anions ($n > Z_0$, for real Z_0).

IV. GEOMETRY-INDEPENDENT CONSTRAINTS BASED ON BOUNDS TO THE LIMIT TRAJECTORY: APPLICATION TO DIATOMIC MOLECULES

Diatomic molecules provide the simplest examples useful in the study of the properties of the ${}^N\mathbf{Z}$ space, since they possess rotational symmetry, hence the scalar $r = \|\mathbf{r}\|$ is sufficient to describe their geometry.

To test the results derived in Sec. III we will consider first two simple examples of chemical interest. If we choose $n = Z_0 = 6$, the level set is established taking as a reference the energy of a carbon atom [$E_0(6,6) = E_C$]. In this case the CET's represent six-electron diatomics that have electronic energy equal to E_C , for a given internuclear separation.

Figure 1 displays the region of plane ${}^2\mathbf{Z}$ of interest, and the bounds to the limit trajectory $f_{r_0}(Z_1, \infty)$ given by $L_6(Z_1)$, $U_6(Z_1)$, and $F_6(Z_1)$ [Eqs. (29), (30), and (34), respectively].

Some particular real molecules have been marked with open circles. We have only included those bordering the limit boundary because they represent the critical tests for our results. Moreover, they are the cases of greater interest when providing constraints for electronic energy hypersurfaces. In fact, their study has been the main motivation of some recent developments in the study of level set topology.⁶

According to Sec. III, from Fig. 1, we expect without any further calculation, the following inequalities for electronic ground states:

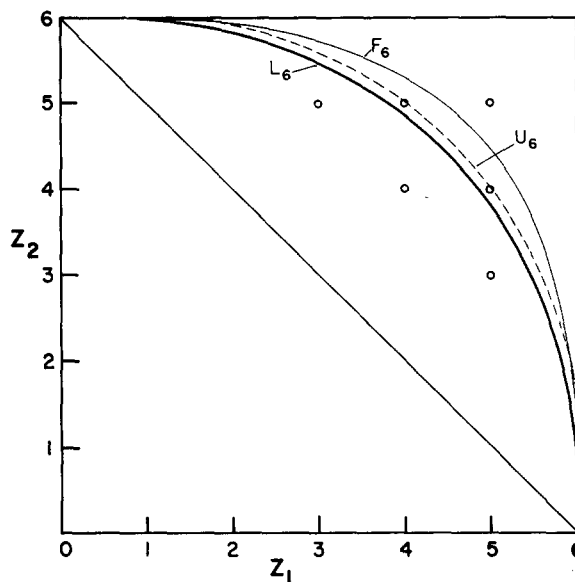


FIG. 1. Approximations to the limit CET for the level set defined on the ${}^2\mathbf{Z}$ space of molecules isoelectronic to carbon. (Although hardly noticeable in the figure, curves U_6 and F_6 do indeed cross inside the square; see Sec. III.)

$$\lim_{r \rightarrow \infty} E_e(\text{LiB}^{2+}) > E_C,$$

$$\lim_{r \rightarrow \infty} E_e(\text{Be}_2^{2+}) > E_C,$$

$$E_e(\text{B}_2^{4+}) < E_C \quad \text{for all } r, \quad (39)$$

furthermore, we can expect that if the electronic energy of BBe^{3+} can reach E_C , it must occur at a very large separation r .

To test whether the previous predictions are true, we simply calculate the limit of the molecular electronic energy for $r \rightarrow \infty$; this can be done by making use of the Hartree-Fock energies of isolated atoms.²⁸ Table I displays the results for the molecules in Eq. (39), among others. Taking into

TABLE I. Test of the limit boundary for the C isoelectronic sequence of diatomic molecules: Comparison of molecular electronic energies at infinite separation with respect to the reference value $E_C = E_0(6,6) = -37.700\ 68$ a.u. (Ref. 28).

\mathbf{Z}	Array	$E_e(\mathbf{Z}, r_\infty)^a$	Region ^b
(3,4)	Li + Be ⁺	-21.711 38	(ii)
	Li ⁺ + Be	-21.808 94	
(4,4)	Be ⁺ + Be ⁺	-28.557 36	(ii)
	Be + Be ²⁺	-28.186 88	
(3,5)	Li + B ²⁺	-30.813 50	(ii)
	Li ⁺ + B ⁺	-31.477 15	
(4,5)	Li ²⁺ + B	-29.033 97	(iii)
	B + Be ³⁺	-32.533 97	
	B ⁺ + Be ²⁺	-37.855 09	
	B ²⁺ + Be ⁺	-37.659 48	
(5,5)	B ³⁺ + Be	-36.561 04	(i)
	B ²⁺ + B ²⁺	-46.761 60	
	B ⁺ + B ³⁺	-43.233 30	
	B + B ⁴⁺	-37.033 97	
(6,1)	C ⁺ + H	-37.804 50	(i)

^a Hartree-Fock energies in a.u. (Ref. 28).

^b See Sec. III.

account that the electronic energy is maximum at $r \rightarrow \infty$, Table I allows one to arrive to the following conclusions:

(a) The limit $r \rightarrow \infty$ of the electronic energy of LiB^{2+} and Be_2^{2+} lies above E_C . Due to the fact that $Z_1 + Z_2 > 6$ in both cases, it is evident that the limit of the energy for $r \rightarrow 0$ lies below E_C . Consequently, both energy curves cross E_C as expected from our results.

(b) The limit $r \rightarrow \infty$ of the electronic energy for B_2^{4+} lies below E_C , except if the dissociation takes place as $\text{B} + \text{B}^{4+}$. Of course, that is not an expected dissociation channel for a diatomic molecule in its ground state. Accordingly, the energy curve as a whole is lower than E_C , and the bound

$$E_{\text{Ne}^{6+}} \leq E_e(\text{B}_2^{4+}) < E_C,$$

holds for all geometries.

It is worth mentioning that our model fixes beforehand the number of electrons related to each atom in the limit of infinite separation. In particular, if $Z_1 = Z_2$ we have $n_1 = n_2 = n/2$. Then it is not surprising that certain arrays of atoms and ions do not fit the bounds provided to the limit trajectory; those arrays are always improbable and are not the natural dissociation channels for a ground state. As a result, our approach restricts the bound only to the accessible dissociation scheme.

(c) Some reasonable dissociation schemes for BBe^{3+} lie above E_C , while others below, but always very near E_C . This confirms completely our prediction about all molecules lying between the upper and lower bounds to $f_{r_0}(Z_1, \infty)$.

Table II shows the numerical Hartree–Fock results for the limit of infinite separation of several molecules of interest, isoelectronic to N . Once again, the last column displays the predicted location of the molecules in the regions discussed in Sec. III, according to the different limit CET. A careful analysis of the results included in the table reveals that all the predictions are correct. In particular, we find the following bound,

$$E_{\text{Mg}^{3+}} \leq E_e(\text{C}_2^{5+}) < E_N,$$

for all internuclear separations.

TABLE II. Test of the limit boundary for the N isoelectronic sequence of diatomic molecules using the reference value $E_N = E_0(7,7) = -54.426\,02$ a.u. (Ref. 28).

Z	Array	$E_e(Z, r_\infty)^a$	Region ^b
(5,5)	$\text{B} + \text{B}^{3+}$	-46.524 72	(ii)
	$\text{B}^+ + \text{B}^{2+}$	-47.623 35	
(4,6)	$\text{C} + \text{Be}^{3+}$	-45.700 68	(ii)
	$\text{C}^+ + \text{Be}^{2+}$	-50.917 04	
	$\text{C}^{2+} + \text{Be}^+$	-50.699 46	
	$\text{C}^{3+} + \text{Be}$	-49.312 12	
(5,6)	$\text{C} + \text{B}^{4+}$	-50.200 68	(iii)
	$\text{C}^+ + \text{B}^{3+}$	-59.295 25	
	$\text{C}^{2+} + \text{B}^{2+}$	-59.801 58	
	$\text{C}^{3+} + \text{B}^+$	-58.980 33	
	$\text{C}^{4+} + \text{B}$	-56.906 02	
(6,6)	$\text{C} + \text{C}^{5+}$	-55.700 68	(i)
	$\text{C}^+ + \text{C}^{4+}$	-69.676 55	
	$\text{C}^{2+} + \text{C}^{3+}$	-71.158 56	

^aHartree–Fock energies in a.u. (Ref. 28).

^bSee Sec. III.

As discussed in the last section, it can be expected that the bounds to the level set boundary are still valid for series built from $n = Z_0$. This possibility is particularly interesting because it allows one to use our results for making predictions about ionization processes in molecules. To give a simple example of how this analysis can be accomplished, let us consider an n -electron diatomic molecule AB . The ionization process:



can take place spontaneously if there exists r^* such that

$$E_e(\text{AB}, r^*) = E_e(\text{AB}^+, r^*). \quad (40)$$

In such a case AB is not stable. It would be of importance then to know if a given molecule AB can cross the electronic energy curve of the molecule AB^+ , for a given conformation. This can be easily deduced if we take as reference energy

$$E_0 = E_e(\text{AB}^+, r^*), \quad (41)$$

with r^* the distance of interest (e.g., the equilibrium distance of AB^+). To apply the results of Sec. III we need Z_0 such that

$$E_0(Z_0, n) = E_e(\text{AB}^+, r^*), \quad (42)$$

for the determination of the nuclear charge of a virtual n -electron atom having the same energy as the $(n-1)$ -electron molecule AB^+ at r^* . This can be calculated for several values of n by using the abundant and accurate information obtained from DFT and the $1/Z$ and $n^{-1/3}$ power series expansions for atoms (see, for example, Refs. 17 and 22).

As an illustration let us consider the simple case $\text{A} = \text{B} = \text{H}$. Let us analyze then, on geometrical grounds, whether the electronic energy of H_2 can reach the electronic energy of H_2^+ at the equilibrium length of the latter ($r^* \approx 2$ a.u.). Even though this example is a simple one, it is one of the less favorable cases to test our approach, for it corresponds to both Z_0 and n low. In this case we have²⁹ $E_e(\text{H}_2^+, r^*) \approx -1.101\,21$ a.u., and using the extensive results in Ref. 30 to solve Eq. (42) ($n=2$) we get $Z_0 \approx 1.335\,441\,8$. With this last value we find

$$L_{Z_0}(1) \approx 0.992\,23, \quad U_{Z_0}(1) \approx 1.013\,05, \quad (43)$$

what indicates that the point $\mathbf{Z} = (1,1)$ (i.e., H_2) is very narrowly enclosed between the approximate upper and lower bounds to the limit trajectory. Result (42) implies that the process $\text{H}_2 \rightarrow \text{H}_2^+ + e^-$ can hardly take place spontaneously because the curves should be expected to cross only at large internuclear distances for H_2 . Of course this conclusion is true, owing to the fact that $E_e(\text{H}_2, r) = E_e(\text{H}_2^+, r)$ for $r \approx 10$ a.u.

This elementary example illustrates two interesting facts:

(i) We can expect that the constraints derived for the limit boundary are also valid for low n and Z_0 values.³¹

(ii) Our procedure allows the discussion of molecular ionization processes. In this case we must compare two molecules of different number of electrons by using the space $^N\mathbf{Z}$ corresponding to the isoelectronic sequence of one of them; this calculation can be accomplished easily by finding the

"pseudocharge" Z_0 of an atom, isoelectronic to one of the molecules, whose energy is equal to the electronic energy of the other molecule of interest.

V. FURTHER APPLICATIONS: TRIATOMIC MOLECULES

The case of triatomic molecules can be analyzed as simply as the examples discussed in the previous section. However, in this case the 3Z space does not have in general the symmetry we found for diatomic molecules. Consequently, it must be noticed that all the vectors obtained by permutation of components of a given vector Z represent in general different molecular arrays.

As a representative illustration, Table III displays the results obtained for a family of triatomic molecules isoelectronic to carbon. The last column represents the location of them in 3Z according to the bounds discussed in Sec. III. The next column shows the Hartree-Fock energy for the limit of pairwise-infinite separation.

It is easily seen that all our predictions hold for all the molecules considered, whenever an appropriate ground-state channel for dissociation is chosen:

(i) The molecules Be_3^{6+} and Li_2B^{5+} can eventually reach the energy of a carbon atom, but at very large distances.

(ii) The molecules BBeli^{6+} and Be_2B^{7+} are bounded by E_C from above:

$$E_{\text{Mg}^{6+}} \leq E_e(\text{BBeli}^{6+}) < E_C,$$

$$E_{\text{Al}^{7+}} \leq E_e(\text{Be}_2\text{B}^{7+}) < E_C.$$

The procedure can then be applied to any sort of molecules and it provides always geometry-independent bounds for the molecular electronic energy in terms of atomic energies. As it has been shown, the method is straightforward

and allows to build the level set with a minimum of computation. Further examples can be easily tested applying the results of Sec. III to discuss the molecules considered in Ref. 6.

VI. FURTHER COMMENTS AND CONCLUSIONS

There are some remarkable consequences of the above results in relation to the atomic ionization potentials. In this section we shall discuss them and their implications for the limit boundary of a level set.

For the sake of simplicity let us consider a two-dimensional space 2Z and let us suppose that a level set is defined by $E_0(Z_A, Z_A)$ with A an arbitrary neutral atom. As a consequence, the molecule AHe^{2+} , isoelectronic to A, can be represented by a point in 2Z lying exactly on one of the sides of a Z_A -length square. Of course that point lies above the curve $F_{Z_A}(Z_1)$, but it will be above $U_{Z_A}(Z_1)$ for certain Z_A values. Accordingly, we know that a species like AHe^{2+} must have an electronic energy lower than $E_0(Z_A, Z_A)$, or at most very similar. Let us assume as a working hypothesis that this energy is always lower than $E_0(Z_A, Z_A)$, for all internuclear separations:

$$E_0(Z_A, Z_A) > E_e(\text{AHe}^{2+}, r_\infty) > E_e(\text{AHe}^{2+}, r). \quad (44)$$

Two inequalities can be deduced from Eq. (44):

$$E_0(Z_A, Z_A) - E_0(Z_A, Z_A - 1) > E_0(2, 1) = E_0(\text{He}^+),$$

$$E_0(Z_A, Z_A) - E_0(Z_A, Z_A - 2) > E_0(2, 2) = E_0(\text{He}).$$

That is,

$$I_1 < |E_0(\text{He}^+)| = 2, \quad (45a)$$

$$I_1 + I_2 < |E_0(\text{He})| = 2.86... , \quad (45b)$$

where I_i is the i th ionization potential of atom A. Using the results of Hartree-Fock electronic energies,²⁸ it is easily seen that inequalities (45) are true for all the elements of the periodic table ($Z_A > 2$).

The last result indicates that our working hypothesis holds (i.e., the opposite hypothesis is false), and that it would be possible to find an upper bound $U'_{Z_0}(Z_1)$ to the limit trajectory with the property $U'_{Z_A}(Z_A) \leq 2$, for $Z_A > 2$. From this result, a reasoning similar to that leading to Eq. (45b) implies

$$\sum_{i=1}^n I_i < |E_0(n, n)|, \quad (46)$$

i.e., the sum of the first n -ionization potentials of an atom of nuclear charge Z_A ($Z_A > 2$) is bounded from above by the absolute value of the ground state energy of the atom of nuclear charge $Z = n$ ($n \geq 2$). Result (46) is again verified throughout the periodic table, using data from Ref. 28.

It is worth mentioning that for the special case of $n = 1$, inequality (46) has 10 exceptions in the periodic table: He, F, Ne, Ar, Eu, Gd, Tb, Dy, Ho, and Er. Consequently, the species AH^+ , isoelectronic to A, do not necessarily have lower electronic energies than that of atom A. This shows that the "true" limit trajectory $f_{r_0}(Z_1, \infty)$ should fulfill the inequality $1 < f_{r_0}(Z_1, \infty) < 2$ for all Z_A , changing probably in this range with the filling of new shells. Of course these characteristics cannot be explained solely on the grounds of

TABLE III. Test of the limit boundary for the C isoelectronic sequence of triatomic molecules [$E_0(6, 6) = -37.700\,68$ a.u. (Ref. 28)].

Z	Array	$E_e(Z, r_\infty)^a$	Region ^b
(5,3,2)	$\text{B}^{4+} + \text{Li} + \text{He}$	-22.7941	(ii)
	$\text{B}^{3+} + \text{Li}^+ + \text{He}$	-32.0867	
	$\text{B}^{2+} + \text{Li}^{2+} + \text{He}$	-30.7422	
	$\text{B}^{2+} + \text{Li}^+ + \text{He}^+$	-32.6154	
	$\text{B}^{3+} + \text{Li} + \text{He}^+$	-31.4234	
(4,4,3)	$\text{Be}^{2+} + \text{Be}^{3+} + \text{Li}$	-29.0452	(ii)
	$\text{Be}^{2+} + \text{Be}^{2+} + \text{Li}^+$	-34.4597	
	$\text{Be}^{2+} + \text{Be}^+ + \text{Li}^{2+}$	-32.3912	
	$\text{Be}^+ + \text{Be}^{3+} + \text{Li}^+$	-29.5133	
	$\text{Be}^{2+} + \text{Be}^{2+} + \text{Be}^{2+}$	-40.8376	
(4,4,4)	$\text{Be}^+ + \text{Be}^{2+} + \text{Be}^{3+}$	-35.8912	(iii)
	$\text{Be} + \text{Be}^{3+} + \text{Be}^{3+}$	-30.5743	
	$\text{Li}^+ + \text{Li}^+ + \text{B}^{3+}$	-36.4599	
(5,3,3)	$\text{Li}^{2+} + \text{Li}^{2+} + \text{B}^+$	-33.2426	(iii)
	$\text{Li}^+ + \text{Li}^{2+} + \text{B}^{2+}$	-35.1154	
	$\text{Be}^{3+} + \text{B}^+ + \text{Li}^{2+}$	-36.7426	
(5,4,3)	$\text{Be}^{2+} + \text{B}^{2+} + \text{Li}^{2+}$	-41.4933	(i)
	$\text{Be}^+ + \text{B}^{3+} + \text{Li}^{2+}$	-40.7694	
	$\text{Be}^{3+} + \text{Be}^{3+} + \text{B}^+$	-40.2426	
(5,4,4)	$\text{Be}^{2+} + \text{Be}^{3+} + \text{B}^{2+}$	-44.9933	(i)
	$\text{Be}^{2+} + \text{Be}^{2+} + \text{B}^{3+}$	-49.2158	

^aHartree-Fock energies in a.u. (Ref. 28).

^bSee Sec. III.

level set topology ideas, and they will be the subject of a forthcoming study.

To summarize the above, we have shown in this paper that all the ground-state inequalities deduced previously in level set topology of molecular electronic energy^{5,6} can be found through simple geometrical arguments from the properties of the limit boundary of the level set, using reliable approximations from DFT. The analysis is straightforward and can be easily applied to *polyatomic molecules* to provide geometry-independent constraints to molecular energies in terms of *just two* atomic energies. Furthermore, we have shown how the procedure can be applied to obtain information about the *feasibility of certain ionization processes*. Beyond their theoretical interest, all these results are of some importance in computational studies of chemical reaction paths and conformational changes, which can be simplified with the help of global constraints to the entire energy hypersurface.^{32,33}

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