PHYSICAL REVIEW A VOLUME 35, NUMBER 10 MAY 15, 1987

Simple analytic bounds for the electronic energy from level set boundaries of nuclear charge space

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(Received 29 December 1986)

The properties of the level set boundaries in ${}^N\mathbb{Z}$ space are used to determine bounds to the interatomic distances at which the electronic energy of a diatomic molecule reaches a specified value. Bounds to the molecular electronic energy curve are obtained from that result. The procedure is very simple and requires having only an approximate representation for the electronic density function of a single atom (the one taken as a reference to define the level set). In the case of one-electron diatomic molecules we derive a function of the internuclear separation which is a rigorous, nonvariational, upper bound to the electronic energy. The method provides complementary results to those global constraints on electronic energy hypersurfaces previously derived in the context of level set topology.

I. INTRODUCTION

Electronic energy hypersurfaces can be studied in a rather simple way by introducing some functional representations whose properties are basically the same for families of molecules. For an N-atomic molecule, the abstract nuclear charge space ${}^N\mathbb{Z}$ provides a very simple and powerful alternative, suitable for the recognition of relationships that must hold for a large class of systems of interest. In this space each molecule is characterized by a vector whose components are the atomic nuclear charges, for all molecular geometries. Consequently, the analysis of the electronic energy functional in ${}^N\mathbb{Z}$, especially the level set topologization of that space, has allowed us to obtain some useful geometry independent constraints and bounds to the entire hypersurfaces.[1,2]

Z-continuous representations of the energy have been used in several fields (see, for instance, Refs. 2–4, and others quoted therein); of particular importance for us is the original application of such convexity relationships to prove rigorously that the electronic energy always takes its minimum in the united-atom limit.[4–6]

In this paper we will present some new results about bounds to the electronic energy, in particular, for diatomic molecules. In this case, using the properties of the ${}^2\mathbb{Z}$ space, and some properties of *a single atom*, we will derive an implicit lower bound to the interatomic distance at which the molecular electronic energy reaches the value of energy chosen to define the level set. Accordingly, it is meaningful to make here some comments about the results previously discussed in the literature on the subject. As mentioned, the electronic energy has a rigorous lower bound in the limit of the united atom; besides, for N-atomic one-electron molecules it has also been proved that the electronic energy increases monotonically with a uniform (or isotropic) dilatation of the molecular geometry.[4,6] This result, which implies that at the limit of infinite pairwise separation the electronic energy is an upper bound, is supposed to hold for all molecules, however, no proof has been given up till now. Recently we have suggested that one must expect such a bound for all nondegenerate ground states, by making use of some properties of the level set boundaries in ${}^N\mathbb{Z}$.[7] On the other hand, some convexity relationships in ${}^N\mathbb{Z}$ have been used to prove some other bounds for the entire hypersurface of a molecule in terms of atomic energies,[1,2,7] or other molecular hypersurfaces.[8] Although these latter bounds are useful, they can be considered as still weak for many applications. Consequently, it is of importance to derive tighter bounds, if possible, from simple geometrical considerations in ${}^N\mathbb{Z}$ space; in particular, it would be very useful to obtain curves that, while being bounds to the electronic energy, would have the same limit behavior as the function of interest (i.e., the same united-atom and infinite pairwise separation limits for the energy).

In this paper we shall show how some results derived from the level set topologization of the ${}^N\mathbb{Z}$ space can be used to deduce new and stronger bounds to molecular electronic energies. In our case, the constraints to the energy are obtained using the properties of the constant energy trajectories (CET) in ${}^N\mathbf{Z}$ to get lower bounds to the interatomic distances. Of course, these new relations introduce some complications not present in earlier treatments; owing to this, our present discussion will be restricted to diatomic molecules. We should emphasize here that our aim is not to derive bounds for equilibrium distances, but to obtain bounds to the electronic energy curve making use of a formalism that provides bounds for the interatomic distance *corresponding to a given value of electronic energy.* Depending on the nuclear charges and the number of electrons, these distances may or may not be similar to the equilibrium bond length. For instance, for homonuclear neutral diatomics the separations may belong to the repulsive branch of the total energy, when the level set is defined in terms of a neutral atom isoelectronic to the molecule of interest. The properties of the CET's in the ${}^N\mathbb{Z}$ space allow us to obtain such bounds by making use of the properties of a single atom.

The organization of the paper is as follows. In Sec. II we review the basic results about the level set boundaries in ${}^2\mathbf{Z}$, which are necessary for our discussion later. In Sec. III we derive rigorous upper bounds to the electronic energy of one-electron diatomic molecules in the Born-Oppenheimer approximation (from the lower bounds to the internuclear separation at which a given reference value of energy is reached). Several examples are shown as illustration. In Sec. IV we discuss how the results can be extended to many-electron molecules using the density-functional theory. Some examples are shown in the context of the Thomas-Fermi approximation. Conclusions and further extensions of the method are found in Sec. V.

II. PROPERTIES OF LEVEL SET BOUNDARIES IN ${}^2\mathbb{Z}$

Let us consider a diatomic molecule with nuclear charges Z_1 and Z_2 (in general, not necessarily integer), and interatomic distance R. This system can be represented as a point in ${}^2\mathbb{Z}$ space with a vector $\mathbf{Z}=(Z_1,Z_2)$, for all R values. In this approach the electronic energy functional can be regarded as a continuous function of the variables $\mathbf{Z}$ and R.

In the Born-Oppenheimer approximation, the electronic energy of an n-electron diatomic molecule is given by (atomic units are used throughout):

$$E_e(\mathbf{Z},R)=\langle H_e(\mathbf{Z},R)\rangle \ , \tag{1a}$$

$$H_e(\mathbf{Z},R)=T_e+V_{ee}-Z_1Q_1-Z_2Q_2 \ , \tag{1b}$$

$$Q_1=\sum_{i=1}^{n}\|\mathbf{r}_i-\mathbf{R}\|^{-1}, \ \ Q_2=\sum_{i=1}^{n}\|\mathbf{r}_i\|^{-1} \ , \tag{1c}$$

where $\mathbf{r}_i$ stands for the position vector of the ith electron and the expectation values are taken over the electronic coordinates. The origin of coordinates has been chosen arbitrarily on the charge Z_2. All remaining terms in (1) have their usual meaning.

The level sets are defined on ${}^2\mathbb{Z}$ as subsets of vectors $\mathbf{Z}$ satisfying the condition $E_e(\mathbf{Z},R)\geq E_0$, for a given geometry. The constant value E_0 is, in principle, arbitrary, and defines the level set. This reference energy can always be taken as the energy of an n-electron atom of charge Z_0 (in general, noninteger), i.e., $E_0=E_0(Z_0,n)$.

We are now in position to define the *boundary* of the level set as a function in ${}^2\mathbb{Z}$ so that $E_e(\mathbf{Z},R)=E_0(Z_0,n)$, for a given R. Such a function establishes of course a constraint between Z_1 and Z_2 under the condition of having a constant value for the electronic energy; without any loss of generality the boundary can be written as

$$Z_2=f(Z_1,R) \ , \tag{2}$$

where we have omitted all reference to E_0 to keep the notation simpler. With the definition of such boundaries, the ${}^2\mathbb{Z}$ space can be partitioned into subsets and given an algebraic topological structure.[1]

The function $f(Z_1,R)$ represents a constant energy trajectory (CET) in ${}^2\mathbb{Z}$, because, by definition, $E_e(\mathbf{Z},R)$ is invariant to changes in $\mathbf{Z}$ as long as $\mathbf{Z}=(Z_1,f(Z_1,R))$ for all Z_1; i.e.,

$$\partial E_e/\partial Z_1=\partial^2E_e/\partial Z_1^2=\cdots=0 \ . \tag{3}$$

Result (3), together with the Hellmann-Feynman theorem, gives the first derivative for the CET:

$$\begin{aligned} f'(Z_1,R)&=(\partial f(Z_1,R)/\partial Z_1)_R \\ &=-\langle Q_1\rangle_{\mathbf{Z},R}/\langle Q_2\rangle_{\mathbf{Z},R} \\ &=\frac{-\int_\tau d\mathbf{r}\rho(\mathbf{r})/\|\mathbf{r}-\mathbf{R}\|}{\int_\tau d\mathbf{r}\rho(\mathbf{r})/\|\mathbf{r}\|} \ , \end{aligned} \tag{4}$$

where ρ is the one-dimensional marginal density function for the diatomic molecule. Equation (4) indicates clearly that $f(Z_1,R)$ is a monotonously decreasing function of Z_1.

Several rigorous properties can be deduced from Eq. (4) and other basic quantum-mechanical relationships, which characterize $f(Z_1,R)$ completely.[7] The following results hold for polyatomic molecules, even though we will be only concerned here with diatomic ones.

(i) For all bound states, in the limit of isolated atom, the derivative of $f(Z_1,R)$ is bounded in the interval $[-1,0]$:

$$-1=\lim_{R\to 0}f'(0,R)\leq f'(0,R)\leq \lim_{R\to\infty}f'(0,R)=0 \ . \tag{5a}$$

In particular, in the limit of the united atom ($R\to 0$) we have

$$f'(Z_1,0)=-1 \ \text{ for all } \ 0\leq Z_1\leq Z_0 \ . \tag{5b}$$

These results imply that $f(Z_1,R)\geq Z_0-Z_1$ for all Z_1. Equations (5) provide an alternative proof of the bounds discussed by Mezey;[1] in particular, it is clear that for all $Z_2<Z_0-Z_1$ the electronic energy is higher than the reference value E_0.

(ii) For the lowest nondegenerate eigenstate belonging to each of the irreducible symmetry representations of the Hamiltonian, the CET's are concave-from-below functions.

Taking into consideration that the ground-state energy of one-electron diatomic (represented simply by vector $\mathbf{Z}$) is a monotonously increasing function of the interatomic distance,[4,6] then, for a given value of E_0 satisfying $E_e(\mathbf{Z},0)\leq E_0\leq E_e(\mathbf{Z},\infty)$, there is one and only one CET $f(Z_1,R)$ containing $\mathbf{Z}$, with $0\leq Z_1\leq Z_0$, $Z_0-Z_1\leq Z_2\leq Z_0$. From this result we conclude that the following theorem holds.

Theorem 1. Let $E_e(\mathbf{Z},R)$ be the nondegenerate ground state of a one-electron diatomic molecule in the Born-Oppenheimer approximation. Let $\{f(Z_1,R)\}$ be the family of infinitely many CET's associated with a reference value $E_0(Z_0,n)$, each of which is related to a different internuclear separation R. Then, for all vectors $\mathbf{Z}$, with $0\leq Z_1\leq Z_0$, $Z_0-Z_1\leq Z_2\leq Z_0$, the set is bounded by the boundaries corresponding to $R=0$ and $1/R=0$ (lower and upper bounds, respectively), and no crossing or osculation takes place between two of such functions; that is,

$$f(Z_1,0)<f(Z_1,R)<f(Z_1,R')<f(Z_1,\infty) \ , \tag{6}$$

with R,R' both finite, nonzero, and $R'>R$.

Theorem 1 holds also for one-electron polyatomic molecules if the family of trajectories is defined through only one scalar parameter characterizing a uniform dilatation from a given initial geometry.[4,7] Besides, strong arguments suggest that it should still hold for many electron molecules.[7,9] A corollary of Theorem 1 follows immediately.

Corollary 1. $f'(0,0) < f'(0,R) < f'(0,R') < f'(0,\infty)$, for R and R' finite, nonzero, and $R' > R$.

This last result shows that for a given value $m \in (-1,0)$ there is one and only one interatomic distance R such that $f'(0,R) = m$. Consequently, the function $f'(0,R)$ can be used to introduce a sort of R-dependent measure of the points in ${}^{N}\mathbb{Z}$ space. This simple idea is the key for the discussion in Secs. III and IV. It is worth noticing that, whereas $f'(Z_1,R)$ is a function standing for an infinite number of molecules, its limit $f'(0,R)$ is a *single-atom property.* This advantageous characteristic, together with Corollary 1, will allow us to obtain simple, fully geometrical, nonvariational, bounds to the electronic energy of a large class of molecules.

III. LOWER BOUNDS TO R AND UPPER BOUNDS TO THE ELECTRONIC ENERGY

As it was discussed in Sec. II, the level set boundaries are confined to a subset of ${}^{2}\mathbb{Z}$ given by $0 \le Z_1 \le Z_0$, $Z_0 - Z_1 \le Z_2 \le Z_0$. In the case of diatomic molecules the abstract nuclear charge space possesses an additional symmetry because two vectors like $\mathbf{Z} = (Z_1, Z_2)$ and $\mathbf{Z}' = (Z_2, Z_1)$, derived through a permutation of nuclei, identify the same system. Consequently we have

$$E_e(\mathbf{Z},R) = E_e(\mathbf{Z}',R) \; , \tag{7}$$

a result that does not necessarily hold for polyatomic molecules. Accordingly, only the subset,

$${}^{2}\mathbb{Z}' = \{\mathbf{Z} \in {}^{2}\mathbb{Z} : 0 \le Z_1 \le Z_0, \max(Z_0 - Z_1, Z_1) \le Z_2 \le Z_0\} \; , \tag{8}$$

needs to be studied to determine all the relevant features of the system.

Let $\mathbf{Z}^* = (Z_1^*, Z_2^*) \in {}^{2}\mathbb{Z}'$ be a one-electron diatomic molecule. If its electronic energy is fixed to be equal to $E_0(Z_0,n)$ of atom Z_0, then its internuclear distance R is unique, but in general unknown. As shown before there is one and only one CET $f(Z_1,R)$ that passes simultaneously through $\mathbf{Z}^*$ and $\mathbf{Z}_0 = (0, Z_0)$, and then there is one and only one value $f'(0,R)$ that can be related to the vector $\mathbf{Z}^*$.

The curvature properties of the CET's, mentioned in Sec. II, imply that

$$f(Z_1,R) > Z_0 + Z_1(Z_2^* - Z_0)/Z_1^* , \quad 0 < Z_1 < Z_1^* \; , \tag{9}$$

and consequently,

$$f'(0,R) > (Z_2^* - Z_0)/Z_1^* \; . \tag{10}$$

Let us define now a new distance x so that

$$f'(0,x) = (Z_2^* - Z_0)/Z_1^* \; ; \tag{11}$$

invoking then the Corollary 1 for the monotonicity of the derivatives, from Eqs. (10) and (11), we get a *lower bound* to the unknown internuclear separation R, determined by $E_e(\mathbf{Z},R) = E_0(Z_0,1)$, that is,

$$x < R \; . \tag{12a}$$

Using the monotonicity of the electronic energy,[4] the inequality (12a) implies

$$E_0(Z_0,1) > E_e(\mathbf{Z}^*,x) \; . \tag{12b}$$

Equations (12) are our main results. They provide valid bounds (in the Born-Oppenheimer approximation) for one-electron diatomic molecules, that are supposed to hold also for many-electron molecules by extension of Theorem 1.[7,9] In addition, Eqs. (12) also provide some information of interest on the total energy $\varepsilon_t(\mathbf{Z},R)$, obtained upon adding the internuclear repulsion to the electronic energy $E_e(\mathbf{Z},R)$. From Eq. (12b) we get, for the reference energy E_0 previously considered,

$$\varepsilon_t(\mathbf{Z}^*,x) < E_0(Z_0,1) + Z_1^* Z_2^* / x \; , \tag{13}$$

where Z_0 and x are related through Eq. (11). If we now choose a reference value ε_{ref} for the total energy and determine the constants x^* and Z_0^* so that Eq. (11) and the condition

$$\varepsilon_{\text{ref}} = E_0(Z_0,1) + Z_1^* Z_2^* / x \tag{14}$$

are simultaneously satisfied, then we have

$$\varepsilon_t(\mathbf{Z},x) < \varepsilon_{\text{ref}}, \quad \text{for all } x \ge x^* \; . \tag{15}$$

That is, x^* provides an upper bound to the internuclear separation at which the above energy inequality is violated, e.g., where the total energy ε_t equals the reference value ε_{ref}. Relations like (15) may be useful to provide bounds for the instability and stability regions of variable R for the ground state of a diatomic molecule. Some previous results, involving the total energy of diatomic molecules in a Z-continuous representation, have been given, using a different approach, aimed at establishing relations for bond strengths of various hydrides,[3] and for several spectroscopic constants of isoelectronic sequences of molecules.[10-12]

In what follows of this section we want to show how the new results are applied to one-electron molecules. In this latter case it is trivial to obtain the reference charge Z_0 which defines the level set; if $\mathbf{Z}^*$ is the molecule of interest we have

$$Z_0 = (-2E_0)^{1/2} \; , \tag{16a}$$

for the singlet ground state, where

$$-(Z_1^* + Z_2^*)^2 \le 2E_0 \le \min(-Z_1^{*2}, -Z_2^{*2}) \; . \tag{16b}$$

At the limit of the united atom the electronic density is fixed completely by Z_0; in our case it is evident that

$$\lim_{Z_1 \to 0} \rho(\mathbf{r}) = Z_0^3 e^{-2Z_0 r}/\pi, \quad r = \|\mathbf{r}\| \; . \tag{17}$$

By substituting (17) into (4), and then into Eq. (11), we obtain the lower bounds to the interatomic distances R [Eq. (12a)], for any one-electron diatomics, by taking the only real positive solution of the following transcendent equation:

$$(Z_2^* - Z_0)/Z_1^* = [e^{-2Z_0 x}(1 + 2Z_0 x + 2Z_0^2 x^2) - 1]/Z_0 x - e^{-2Z_0 x}(1 + 2Z_0 x) \; , \tag{18}$$

where the level set reference charge is determined by means of Eqs. (16). On the other hand, for each value of x, the value Z_0 obtained from (18) gives an upper bound to $E_e(\mathbf{Z}^*,x)$ using Eq. (16a):

$$U(x)=E_0(Z_0(x),1)=-Z_0(x)^2/2\geq E_e(\mathbf{Z}^*,x)\ . \qquad (19)$$

Taking into consideration that $\mathbf{Z}^*\in{}^2Z'$ (then $Z_2^*\geq Z_1^*$), it is immediate to deduce from Eq. (18) that

$$\lim_{Z_0\to(Z_1^*+Z_2^*)} x=0,\quad \lim_{Z_0\to Z_2^*}(1/x)=0\ , \qquad (20a)$$

that is consistent with the results for the united-atom and infinite pairwise separation limit behavior of $f'(0,x)$ [Eq. (5a)]. This shows that the curve $U(x)$ obtained from Eqs. (18) and (19) is an upper bound having the same $x=0$ and $1/x=0$ limits as the exact electronic energy. Besides, it can be shown that $U(x)$ possesses also the same analytic structure as the exact electronic energy when approaching either limit in (20a). Upon expanding Z_0 in power series of x [whose coefficients are easily determined from Eq. (18)], and then substituting it into Eq. (19), we deduce the following result for the upper bound $U(x)$ in the limit of united atom:

$$\begin{aligned}U(x)=&-(Z_1+Z_2)^2/2+(\tfrac{2}{3})Z_1(Z_1+Z_2)^3x^2\\&-(\tfrac{2}{3})Z_1(Z_1+Z_2)^4x^3+\cdots\ . \end{aligned}\qquad (20b)$$

Comparison of the second and third terms of the right-hand side of Eq. (20b) with the exact result (Ref. 13 and others quoted there) shows that they coincide with the latter if $Z_1(Z_1+Z_2)^3$ is replaced by $Z_1Z_2(Z_1+Z_2)^2$ in the second term and $Z_1(Z_1+Z_2)^4$ by $Z_1Z_2(Z_1+Z_2)^3$ in the third. These results confirm that $U(x)$ provides an upper bound to the exact electronic energy and behaves similarly to the latter in the neigborhood of the united atom limit. On the other hand, we get from Eqs. (18) and (19) the first terms for the expansion of $U(x)$ about $1/x=0$:

$$U(x)=-Z_2^2/2-Z_1/x+Z_1^2/2Z_2^2x^2+\cdots\ , \qquad (20c)$$

which reveals again a structure similar to the exact result while providing an upper bound.

It is worth mentioning that one can expect beforehand that the quality of the bounds will not be the same for all molecules; the reason is very simple: The larger is the difference $Z_2^*-Z_1^*$, the tighter is the bound given by Eq. (10). Accordingly, results will be better for heteronuclear than for homonuclear diatomics. In particular, $H_2{}^+$ can be considered as the strongest test for our method, so we have chosen it as the first illustrative example.

Figure 1 displays the results obtained for the latter molecule ($Z_1^*=Z_2^*=1$) with Eqs. (18) and (19), compared with the exact numerical electronic energy.[14,15] As the critical example, the approximation obtained can be considered as very satisfactory, provided our bound is nonvariational but simply based on basic geometric properties of CET in abstract nuclear charge space. The evaluation of $U(x)$ is straightforward for all molecules, and it represents an approach independent from the usual linear combination of atomic orbitals—molecular orbital (LCAO-MO) method, which makes use of similar information.

Table I shows the lower bounds obtained for the internuclear separation corresponding to some selected electronic energy values of several molecules. The results follow the behavior already mentioned: The accuracy increases with Z_2 in the series of molecules $(Z_2\,\mathrm{H})^{Z_2+}$ and $(Z_2\,\mathrm{He})^{(Z_2+1)+}$. For $R>2$ and $Z_2-Z_1>1$, the simple bounds obtained by the above method, relying only on atomic properties (in the present case on hydrogenlike atoms), are surprisingly good.

The results derived in this section involve no approximation, and represent new constraints to electronic energy curves based on the level set topological structure of ${}^2\mathbf{Z}$.

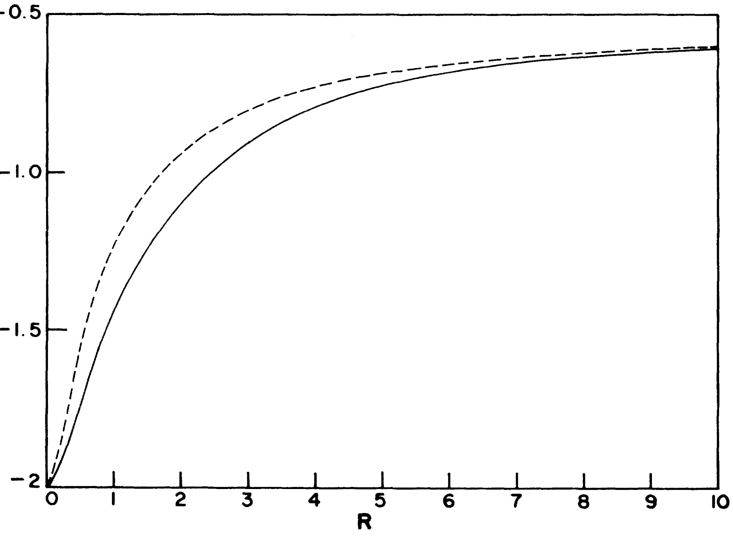

FIG. 1. Upper bound $U(x)$ for the electronic energy of the ground state of $H_2{}^+$ (in a.u.). — — —, $U(x)$ [Eqs. (18) and (19)]; and ——, exact numerical results (Ref. 14).

TABLE I. Lower bounds x, to the internuclear separation R, for several one-electron diatomic molecules, at which separation the molecular electronic energy equals the reference energy value (see Sec. III). (All values in atomic units.)

Molecule	$-E_e(R=2)^{a}$	x^{b}	$-E_e(R=4)^{a}$	x^{b}	$-E_e(R=6)^{a}$	x^{b}
H_2^{+c}	1.102 634 2	1.303 505	0.796 084 9	3.019 887	0.678 635 7	5.201 320
HeH^{2+}	2.512 175	1.844 85	2.2506	3.8761	2.1668	5.8763
LiH^{3+}	5.02±0.01	1.87±0.03	4.75±0.01	3.9±0.1		
He_2^{3+}	3.183±0.002	1.51±0.01	2.525±0.005	3.61±0.03		
$LiHe^{4+}$	5.515±0.005	1.87±0.01	5.005±0.005	3.86±0.04		

[a] Exact numerical electronic energy for a given in internuclear separation R (Ref. 30).

[b] Lower bounds from Eqs. (16) and (18).

[c] Exact numerical results for $E_e(\mathbf{Z},R)$ taken from Ref. 14.

In the case of many-electron molecules the same exact treatment is no longer possible, because no analytic exact expression can be given for $\rho(\mathbf{r})$. However, the bounds can be obtained in an approximate framework as shown in Sec. IV.

IV. EXTENSION OF THE BOUNDS TO MANY-ELECTRON DIATOMICS

The results obtained in Sec. III can be used to provide upper bounds to the electronic energy as long as an approximation to the atomic electron density $\rho(\mathbf{r})$ is available for substitution into Eqs. (4) and (11). Although this represents a potentially successful application, it is rather complicated and cannot be accomplished analytically. This problem will not be discussed in the present paper.

The analysis of many-electron molecules can be accomplished more easily if we rewrite the equations previously deduced, in terms of another function rather than the electronic density. The starting point is the Poisson equation for the atomic electrostatic potential $\varphi(r)$:

$$\Delta\varphi(r)=-4\pi\rho_0(r) , \tag{21a}$$

where $\rho_0(r)$ stands for the radial charge density of the atom with reference charge Z_0 ($Z_1=0$ in Sec. III). Defining the screening function $\phi(r)$ as

$$\varphi(r)=-Z_0\phi(r)/r , \tag{21b}$$

Eq. (21a) leads to

$$\rho_0(r)=Z_0\phi''(r)/4\pi r , \tag{21c}$$

where $\phi(r)$ satisfies the boundary conditions $\phi(0)=1$ and $\phi(\infty)=0$. Substituting (21c) into (4), one obtains the following expression for the derivative of the CET:

$$f'(0,R)=[1-\phi(R)]/R\phi'(0) , \tag{22}$$

with $\phi'(0)<0$. Equations (11) and (22) allow the determination of a specific lower bound to R: the distance at which the electronic energy of the molecule happens to be equal to $E_0(Z_0,n)$. This bound for an internuclear distance of a *molecule* is determined from the properties of a *single atom*. For a given reference charge Z_0, and for the molecule $\mathbf{Z}^*$ of interest we have

$$1-\phi(x)=x\phi'(0)[Z_2^*-Z_0]/Z_1^* . \tag{23}$$

Equation (22) seems to be especially useful, because it permits the utilization of the result of extensive research done on screening functions like $\phi(r)$. In particular, the density-functional theory provides simple expressions for $\phi(r)$ which allow us to perform most calculations analytically. As an illustrative example, we will consider here the simplest approximation provided by the Thomas-Fermi (TF) model (see, for example, Refs. 6 and 16—18). According to this model, the screening function is related to the density $\rho_0(r)$ as

$$\rho_0(r)=[Z_0\phi(r)]^{3/2}/3(2^{1/2})\pi^2 r^{3/2} . \tag{24}$$

Substitution of this expression into Eq. (21a) shows that $\phi(r)$ is determined by a nonlinear second-order differential equation. In the general case of $n\neq Z_0$ the boundary conditions must be introduced carefully in order to distinguish between atoms and ions (Ref. 19 and others therein). Instead of solving that equation numerically, we will follow the usual procedure consisting of introducing trial screening functions subject to the condition:

$$\int_\tau \rho(\mathbf{r})\,d\mathbf{r}=n . \tag{25}$$

Several analytic representations of $\phi(r)$ are available for atoms and ions (see, for instance, Refs. 20—24), but it is enough for our illustrative purposes to choose the Tietz approximation,[18] which is a most elementary one. In this case we have

$$\phi(r)=(1+Ay)^{-2},\quad y=(128Z_0/9\pi^2)^{1/3}r=br , \tag{26a}$$

where A is determined from the conditions that it should satisfy Eqs. (24) and (25):

$$A=(Z_0^2\pi^2/64n^2)^{1/3} . \tag{26b}$$

The variable y is chosen to be the same as in the dimensionless TF differential equation. Although (26) does not fulfill Csavinszky's variational principle,[24,25] it is known to be a fairly acceptable approximation to the TF field. We will use here Eq. (26) to provide a simple illustration of the implementation of the results in Sec. III to many-electron molecules.

By substituting (26) in (23), we obtain the lower bound to the interatomic distance as the largest positive solution of the following equation:

$$2A^3Mx'^2+A^2(1+4M)x'+2A(1+M)=0\ , \qquad (27)$$

with $M=(Z_2^*-Z_0)/Z_1^*$, and $x'=bx$.

In order to apply Eq. (27) we must introduce the reference energy value E_0 of interest, and obtain the charge Z_0 from it. Of course, in the case of many-electron atoms there is no closed expression for the analytical continuation of $E_0(Z_0,n)$ with Z_0 noninteger; however, this can be done approximately by using the representations of the electronic energy as a continuous function of the nuclear charge and number of electrons, obtained from density-functional theories. In our case we will make use of the results from Tal and Bartolotti[26] based on the superimposed expansions in power series of $1/Z_0$ and $1/n^{1/3}$, which provide a very accurate representation of the Hartree-Fock energies $E_0(Z_0,n)$ for all Z_0 and $n\geq 2$.

It is worth mentioning that there is a particular case of reference energy which can be discussed very easily without using the analytic continuation for noninteger Z_0. If we take $Z_0=n$ in Eq. (27), the distance x will be a lower bound to the internuclear separation for which the electronic energy of our n-electron molecule equals the energy of an n-electron neutral atom. In what follows some examples of the above mentioned two possible applications are shown.

A simple problem that can be studied using Eq. (27) is, of course, the case of two-electron diatomic molecules. Notwithstanding their simplicity, those systems are somewhat critical in our approach, because Eqs. (24) and (26) are known to be more accurate for large n.[16,18] To illustrate briefly the typical results derived following our procedure, we will take H_2 as a working example. Let us consider the molecules H_2^+ and H_2, and let us verify, exclusively from properties of CET's in $^2\mathbf{Z}$, that their electronic energy curves cannot cross. This analysis can be done easily in the following way.

(i) The electronic energy of H_2^+ $[E_e(H_2^+,R)]$ is taken, for a given R, as the reference energy to define the level sets for H_2.

(ii) Then, the noninteger charge Z_0 of a two-electron pseudoatom having as energy the above reference value is determined. This can be done easily using the approximate expressions in Ref. 26.

(iii) From Eq. (27), one can determine the lower bound x to the internuclear distance R' at which the electronic energy of H_2 equals the reference value of energy [i.e., when $E_e(H_2,R')=E_e(H_2^+,R)$ takes place]. If, for the whole range of electronic energy of H_2, it happens to be that $x\geq R$ (that is, $R'\geq R$), then the entire electronic energy curve for H_2 will lie below that of H_2^+. Table II shows the typical results obtained following the above steps. Even though the approximation chosen is crude and elementary, and the bounds are rather loose, the method suffices for showing that the curves cannot cross. It is important to remark here that this sort of constraints for molecular electronic energies, obtained from simple information about a single atom, represents a generalization of those previously derived from properties of the nuclear charge space.[1,2,7] Earlier treatments cannot be applied to the kind of molecules we have compared here.

TABLE II. Comparison of electronic energy curves for H_2 and H_2^+ using the lower bounds for interatomic distances. (In this case the electronic energy of the latter is taken as a reference energy for the former.) (All values in atomic units.)

R	$-E_e(H_2^+,R)^a$	$Z_0{}^b$	x^c
0.0	2.0	1.721 73	0.3774
0.5	1.734 987 9	1.624 32	0.6145
1.0	1.451 786 3	1.511 51	1.0258
1.5	1.248 989 9	1.423 70	1.5210
2.0	1.102 634 2	1.355 75	2.0895
2.47[d]	1.000	1.3053	2.6864

[a]Exact numerical results taken as reference energy (Ref. 14).

[b]Reference charge calculated from $E_e(H_2^+,R)$ using the results of Ref. 26.

[c]Approximate lower bounds to R for H_2 [Eq. (27)].

[d]Interpolation from results in Ref. 14.

In order to determine a lower bound to the interatomic distance at which the electronic energy of a diatomic molecule equals that of an isoelectronic neutral atom, we must know beforehand if that situation is likely to happen. That fact can be predicted accurately using a simple approximate result recently shown:[7] If $\mathbf{Z}^*\in {}^2\mathbf{Z}'$ and $Z_2^*\leq(Z_0^{7/3}-Z_1^{*7/3})^{3/7}$, then one should expect that there exists a finite R at which $E_e(\mathbf{Z}^*,R)=E_0(Z_0,n)$. We use this criterion to choose the appropriate examples to apply the equations shown above.

As an illustrative example we have chosen some 13-electron diatomics (fulfilling the condition of finite R) which are of some interest in atmospheric and interstellar chemistry (Refs. 27—29, and others quoted therein). Results are displayed in Table III. The lower bounds x are valid when compared with full quantum-mechanical calculations in all the cases where the information is available. As mentioned before, the bounds are tighter for heteronuclear diatomics, but can be considered in general as satisfactory. It must be stressed that in the examples chosen here, the distance R corresponds to the repulsive

TABLE III. Approximate lower bounds (in a.u.) for interatomic distances of 13-electron diatomics, taking as electronic energy reference the value $E_0(13,13)=-242.2862$ a.u. of the neutral Al atom (Ref. 31) (Notice that for the various molecules the interatomic separations corresponding to the reference energy fall on the repulsive branch of the total energy.) For bounds corresponding to different values of the reference energy see Sec. IV.

Molecule	x^a	Molecule	x^a
N_2^+	0.076 69	NO^{2+}	0.180 39
CO^+	0.091 74	CF^{2+}	0.223 79
FB^+	0.114 16	BNe^{2+}	0.295 00
$LiNa^+$	0.223 79	$LiMg^{2+}$	0.832 84

[a]Lower bound to the interatomic distance calculated with Eq. (27) (a.u.).

branch in the total electronic energy; for similar examples with lower number of electrons (or with larger molecular charge) that distance is nearer to the internuclear separation at equilibrium. The complete curve representing the upper bound for the above molecules can be built easily following the same procedure already described for the analysis of the molecule H_2. In this case, use should be made of the expressions in Ref. 26 for the extension of the electronic energy of atoms to noninteger nuclear charge values.

V. FURTHER COMMENTS AND CONCLUSIONS

An extension of the rigorous results derived in Sec. III (for one-electron molecules) to many-electron diatomics has been given in Sec. IV employing a simple approximation. The examples provide an elementary illustration of how the original ideas can be applied.

Even though we have considered a crude representation for the atomic charge density, in all the cases the results obtained follow the predicted behavior. This fact suggests that a better representation of $\phi(r)$ in Eq. (23) could lead to an improvement of the results. Notwithstanding that latter possibility should be explored, we believe that the more significant improvements could be achieved if a stronger lower bound to the derivative in Eq. (10) could be found. The development of such a new bound requires the investigation of more detailed analytic properties of the CET's, and work along this line is being done at present in our laboratory.

It is worth mentioning that the study of global constraints for the entire energy hypersurface has been motivated mainly because of their potential use in computer aided synthesis planning and the theoretical analysis of chemical reactions and molecular conformations. In particular, the approach based on the properties of the energy functional in the abstract nuclear charge space has shown to be fruitful to derive simple and general constraints. In this paper we have discussed one of the possible ways along which those constraints can be given a more detailed analytic structure.

ACKNOWLEDGMENT

This work was supported by a research grant from the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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