Lower bounds on equilibrium configurations of diatomic molecular systems

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A simple but rigorous relation is derived that provides uniform lower bounds on the equilibrium internuclear distance R_e where the potential-energy curves of diatomic molecules in the Born-Oppenheimer approximation have a minimum. By employing monotonicity properties and explicit lower bounds on electronic energies, the applications of these R_e bounds to systems with one or two electrons are discussed in detail.

For a diatomic molecule with a given number N of electrons, the behavior of its potential-energy curves (PEC's) and thus, also, its stability properties depend crucially on the involved nuclear charges $Z_A, Z_B > 0$. Varying these charges, on certain Z_A, Z_B intervals, PEC's enjoy global or local minima providing the associated states of the system with stable or metastable equilibrium configurations against (adiabatic) dissociation [1–3]. In particular, if the respective intervals contain physical, i.e., integer, Z_A, Z_B, this allows the formation of bound or quasibound systems. *A priori* information on the location of such equilibrium configurations—such as, e.g., rigorous bounds on the region of internuclear separations R where minima R_e of the considered PEC's can occur—is of interest for theoretical as well as for practical purposes. Whereas for N and Z_A, Z_B fixed, the R_e cannot be bounded from above uniformly for all states, a uniform lower bound on R_e will be established below. Despite its rather simple derivation, the existence of such a lower bound appears to be unnoticed in the literature until Ref. [4] where this type of bound entered as an important tool into the stability analysis of the one-electron molecular ion. In addition to supplying a proper derivation of the lower bound relation, the aim of this note is to study various forms of the bound for specific situations and to compare the resulting values with R_e data from accurate numerical computations.

Assuming the validity of the Born-Oppenheimer approximation, the total molecular Hamiltonian

$$H(R; Z_A, Z_B; \mu) = h(R; Z_A, Z_B; \mu) + Z_A Z_B / R \tag{1}$$

as well as its electronic part

$$h(R; Z_A, Z_B; \mu) = t(\mu) + v(R; Z_A, Z_B) \tag{2}$$

contain the internuclear distance $R = |\mathbf{R}|$; the nuclear charges $Z_A, Z_B > 0$; and the electron mass μ (that eventually will be set to its physical value 1 in atomic units) as parameters. In Eq. (2), t denotes the kinetic-energy operator of the electrons,

$$t(\mu) = \frac{1}{2\mu} \sum_{i=1}^{N} \mathbf{p}_i^2 , \tag{3}$$

and v the potential

$$v(R; Z_A, Z_B) = -\sum_{i=1}^{N} \left[\frac{Z_A}{|\mathbf{r}_i|} + \frac{Z_B}{|\mathbf{r}_i - \mathbf{R}|} \right] + v_{ee}(N) , \tag{4}$$

where the electron-electron repulsion is non-negative $v_{ee} \geq 0$ or absent $v_{ee}(N=1) \equiv 0$ for one-electron systems. The Hamiltonian H (or h) is reduced by subspaces Λ_α of states invariant under irreducible representations of the symmetry group $\mathcal{C}_{\infty v}$. By Eq. (1), the electronic

$$h \psi_{\alpha, \nu} = e_{\alpha, \nu} \psi_{\alpha, \nu} \tag{5}$$

and total energy $E_{\alpha, \nu}$ are related by

$$E_{\alpha, \nu}(R; Z_A, Z_B; \mu) = e_{\alpha, \nu}(R; Z_A, Z_B; \mu) + Z_a Z_B / R ,$$

and we adopt a labeling ν of the states $\psi_\alpha \in \Lambda_\alpha$ that preserves the differentiability of the PEC's $E_{\alpha, \nu}$ and $e_{\alpha, \nu}$ with respect to R. The state in Λ_α with lowest energy will be denoted by $\psi_{\alpha, 0}$, and the (symmetry-unrestricted) ground state by ψ_0.

Let $R_e^{\alpha, \nu}$ be the (smallest) internuclear distance for an equilibrium configuration of the system in state $\psi_{\alpha, \nu}$:

$$R_e^{\alpha, \nu}(Z_A, Z_B; \mu) = \begin{cases} \min\{ R_e \,|\, E_{\alpha, \nu}(\cdot; Z_A, Z_B; \mu) \text{ has a minimum at } R_e \} \\ \infty \text{ if there is no minimum for } E_{\alpha, \nu} . \end{cases} \tag{6}$$

Then the following lower bound holds for $R_e^{\alpha, \nu}$:

$$R_e^{\alpha, \nu} \geq \sup_{0 \leq R \leq R_e^{\alpha, \nu}} [2 Z_A Z_B / |e_{\alpha, 0}(R/2; Z_A, Z_B; \mu)|] . \tag{7}$$

The proof of Eq. (7) rests on a simple combination of the molecular virial theorem, the minimax principle, and a scaling argument. Namely, for $R > 0$, by the virial theorem (cf. Sec. 4.6.16 in Ref. [5]),

$$(dE_{\alpha,\nu}/dR)(R;Z_A,Z_B;\mu) = -(1/R)[-\langle v(R;Z_A,Z_B)\rangle_{\alpha,\nu} - (Z_AZ_B/R) + 2E_{\alpha,\nu}(R;Z_A,Z_B;\mu)]$$
$$= -(1/R)[2\langle t(\mu)\rangle_{\alpha,\nu} + \langle v(R;Z_A,Z_B)\rangle_{\alpha,\nu} + (Z_AZ_B/R)]$$
$$= -(1/R)[\langle h(R;Z_A,Z_B;\mu/2)\rangle_{\alpha,\nu} + (Z_AZ_B/R)] , \tag{8}$$

where $\langle\ \rangle_{\alpha,\nu}$ stands for the expectation value taken within $\psi_{\alpha,\nu}$, i.e., an eigenstate for electron mass μ. The minimax principle followed by a scaling in the mass parameter gives

$$\langle h(R;Z_A,Z_B;\mu/2)\rangle_{\alpha,\nu} \geq e_{\alpha,0}(R;Z_A,Z_B;\mu/2)$$
$$= \tfrac{1}{2}e_{\alpha,0}(R/2;Z_A,Z_B;\mu) . \tag{9}$$

Hence, the condition for a repulsive PEC, $dE_{\alpha,\nu}/dR < 0$, is satisfied if

$$R < 2Z_AZ_B/|e_{\alpha,0}(R/2;Z_A,Z_B;\mu)| , \tag{10}$$

yielding immediately the inequality (7).

Before proceeding to applications, let us extract some more specific bounds from the rather general formulation of Eq. (7). First, since $e_0 \leq e_{\alpha,0}$, the inequality (7) implies that

$$R_e^{\alpha,\nu} \geq \sup_{0 \leq R \leq R_e^{\alpha,\nu}} \left\{ \frac{2Z_AZ_B}{|e_0(R/2;Z_A,Z_B;\mu)|} \right\} . \tag{11}$$

Furthermore, for the ground state the united-atom energy is always below the molecular electronic energies, i.e.,

$$e_0(Z_A+Z_B;\mu) \equiv e_0(0;Z_A,Z_B;\mu) \leq e_0(R;Z_A,Z_B;\mu)$$

(see, e.g., 4.6.14 in Ref. [5]). Therefore, a uniform lower bound on all $R_e^{\alpha,\nu}$ is given by

$$R_e^{\alpha,\nu} \geq 2Z_AZ_B/|e_0(Z_A+Z_B;\mu)| . \tag{12}$$

Improved bounds can be obtained for states for which the electronic PEC of $\psi_{\alpha,0}$ is monotonically increasing in R. Then, starting with $R_{e;0}^{\alpha,\nu} \equiv 0$, by

$$R_{e;k}^{\alpha,\nu} \equiv \frac{2Z_AZ_B}{|e_{\alpha,0}(R_{e;k-1}^{\alpha,\nu}/2;Z_A,Z_B;\mu)|} \tag{13}$$

for $k \geq 1$, an iterative sequence of lower bounds is defined and Eq. (7) says that $\lim_{k\to\infty}(R_{e;k}^{\alpha,\nu}) \leq R_e^{\alpha,\nu}$.

Finally, we note that, as they stand, the preceding relations are of little practical use because in general the exact energies $e_{\alpha,0}$ are unknown. The point is, however, that the inequalities (7) and (11)–(13) remain true if the exact energies are replaced by lower bounds $e_{\alpha,0}^{LB} \leq e_{\alpha,0}$.

For systems with one electron (fixing now $\mu=1$), the united-atom energies are, of course, well known. Hence, by Eq. (12), for all states of the one-electron molecule,

$$R_e^{\alpha,\nu} \geq [4Z_AZ_B/(Z_A+Z_B)^2] = [4\eta/(1+\eta)^2] , \tag{14}$$

where $\eta \equiv Z_B/Z_A$. For the physically most important cases $\eta=1$ (including H_2^+) or $\eta=\tfrac{1}{2}$ (including HeH^{2+}) this gives $R_e^{\alpha,\nu} \geq 1$ or $R_e^{\alpha,\nu} \geq \tfrac{8}{9}$, respectively. Actual values of the smallest possible bond lengths

$$\min_{Z_A,Z_B>0} \{R_e^{\alpha,\nu}(Z_A,Z_B)|Z_B/Z_A = \eta\}$$

for various states of the $\eta=1,\tfrac{1}{2}$ case are collected in Table I. These data are based on accurate *ab initio* computations of the PEC's and the simple scaling properties (in Z_A,Z_B) of the one-electron Hamiltonian (for details, cf. Ref. [3]). In both situations $\eta=1$ and $\tfrac{1}{2}$, the smallest computed R_e is about twice as large as the corresponding uniform lower bound and occurs for the ground state $1s\sigma$ at $Z_A=0.7924$ or $Z_A=0.7499$, respectively, i.e., at charge values below the physical ones. For excited states, the minimal R_e distances are rapidly increasing.

While a detailed interpretation of the data of Table I goes beyond the scope of this paper, it must be pointed out that in Table I we selected states whose PEC's also have a minimum for the physical charge parameters; for these charges, most of the other states are repulsive on the considered R range (i.e., [0,50] or larger, where $Z_A \geq Z_B$ and Z_B is fixed at 1). In contrast to the situation for the tabulated states, in most cases the smallest R_e are assumed for Z_A,Z_B below the values for H_2^+ or HeH^{2+}. Moreover, although from Table I it might appear that the minimum of R_e occurs for charges above those of a corresponding neutral system (viz., $Z_A=Z_B=\tfrac{1}{2}$ if $\eta=1$, or $Z_A=2Z_B=\tfrac{2}{3}$ if $\eta=\tfrac{1}{2}$), for most states this is not true; e.g., for the $2s\sigma$ state $R_e=9.4480$ at $Z_A=Z_B=0.3456$ ($\eta=1$) and $R_e=11.3102$ at $Z_A=2Z_B=0.2508$ ($\eta=\tfrac{1}{2}$).

For one-electron systems, the ground state $1s\sigma$ as well

TABLE I. Minimal R_e for various states of the one-electron molecular system together with the corresponding charge Z_A. For comparison, the R_e for the physical charges $Z_A=1$ or 2 are also given.

$\eta=Z_B/Z_A=\tfrac{1}{1}$		
State	min (R_e)	Z_A	$R_e(Z_A=1)$
$1s\sigma$	1.9524	0.7924	1.9972
$2p\sigma$	8.4363	0.7939	12.5461
$3d\sigma$	7.3395	1.6127	8.3341
$4d\sigma$	17.7680	0.9414	17.8492
$4f\sigma$	20.7331	1.0681	20.9210
$5g\sigma$	16.1158	1.9773	23.9003
$2p\pi$	7.4655	0.7225	7.9307
$4f\pi$	16.6458	1.4079	18.6078
$3d\delta$	16.4496	0.7039	17.9670

$\eta=Z_B/Z_A=\tfrac{1}{2}$		
State	min(R_e)	Z_A	$R_e(Z_A=2)$
$1s\sigma$	2.1309	0.7499	∞
$2p\sigma$	3.8587	1.8392	3.8979
$4f\sigma$	11.3528	2.2785	11.7657
$5g\sigma$	15.8144	2.6521	18.1538
$6h\sigma$	27.9935	2.0389	28.0604
$7i\sigma$	26.3190	3.0811	33.7353
$4f\pi$	16.2058	1.8898	16.4516
$6h\pi$	26.7934	2.4775	28.9799
$5g\delta$	26.9470	1.8064	27.9710

TABLE II. Minimal R_e for the lowest state in the angular momentum $|m| = 1, 2, \ldots, 7$ sectors of the one-electron molecular system together with their reduced values $\min(R_e)/(|m|+1)^2$ and the corresponding charges Z_A.

State	$\eta = Z_B/Z_A = \frac{1}{1}$			$\eta = Z_B/Z_A = \frac{1}{2}$		
	min (R_e)	min $(R_e)/n^2$	Z_A	min (R_e)	min $(R_e)/n^2$	Z_A
$1s\sigma$	1.9524	1.9524	0.7924	2.1309	2.1309	0.7499
$2p\pi$	7.4655	1.8664	0.7225	8.3903	2.0976	0.6425
$3d\delta$	16.4496	1.8277	0.7039	18.8265	2.0918	0.6036
$4f\phi$	28.8828	1.8052	0.6963	33.4677	2.0917	0.5834
$5g\gamma$	44.7523	1.7901	0.6929	52.3248	2.0930	0.5711
$6h\chi$	64.0519	1.7792	0.6913	75.4025	2.0945	0.5629
$7i\psi$	86.7737	1.7709	0.6907	102.7028	2.0960	0.5571
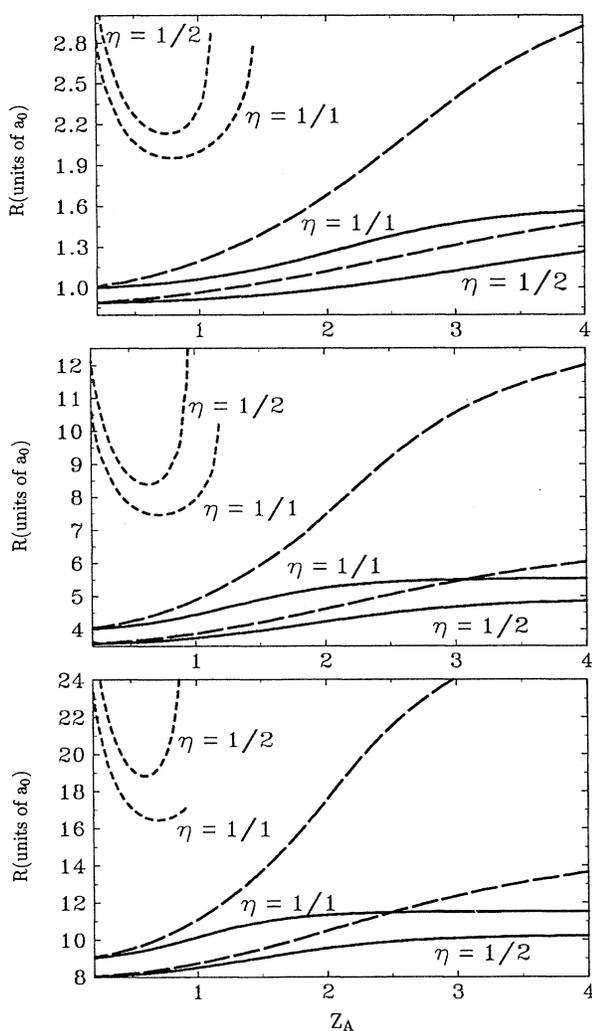
FIG. 1. One-electron system: Lower bound R_e from lower-bound energies $e_{\alpha,0}^{LB}$ (solid curves) and from exact energies $e_{\alpha,0}$ (long-dashed curves) in comparison to exact R_e (short-dashed curves) for $\eta = Z_B/Z_A = \frac{1}{1}, \frac{1}{2}$ and the lowest states in the σ (upper part), π (middle part), and δ (lower part) symmetry sector.

as each lowest state $2p\pi, 3d\delta, 4f\phi, \ldots$ in the $|m| = 1, 2, 3, \ldots$ angular momentum symmetry sector have a monotonically increasing (in R) electronic PEC [6,7]. Hence, in Eq. (13) we can use the appropriate excited level of the united-atom energy and arrive at

$$R_e^{\alpha_m, \nu} \geq 4\eta(|m|+1)^2/(1+\eta)^2 \tag{15}$$

as uniform lower bound for all states having angular momentum $|m|$. In particular, $R_e^{\alpha_m, \nu} \geq (|m|+1)^2$ if $\eta = 1$ or $R_e^{\alpha_m, \nu} \geq 8(|m|+1)^2/9$ if $\eta = \frac{1}{2}$. These bounds should be compared with the computed minimal R_e listed in Table II. By looking at the reduced quantities $\min(R_e)/(|m|+1)^2$, it becomes obvious that the increase of R_e with $n^2 = (|m|+1)^2$ is correctly reflected by the bounds in Eq. (15), while the actual values differ by a factor of about 2.

If $R > 0$, the unknown $e_{\alpha,0}$ must be replaced by lower bounds $e_{\alpha,0}^{LB}$. Falling back on explicit expressions [8] for the $e_{\alpha,0}^{LB}$ we can apply the procedure indicated in the context of Eq. (13) for a further improvement of the R_e bounds. The results are depicted in Fig. 1. Also plotted are lower bounds that follow by inserting the exact (numerical) energies $e_{\alpha,0}$ into Eq. (13). The increasing discrepancy between these curves and the curves obtained with the $e_{\alpha,0}^{LB}$ is due to the decreasing quality of the lower energy bounds for larger R. With sharper bound functions $e_{\alpha,0}^{LB}$ derived, e.g., by taking Temple's inequality [5] in conjunction with test wave functions containing two or more parameters, it would not be hard to raise the R_e bounds on the entire displayed domain to values very close to those from the exact PEC. However, such $e_{\alpha,0}^{LB}$ are no longer representable in simple closed form. On the other hand, as a consequence of monotonically increasing electronic PEC's, the largest lower R_e bounds attainable via Eq. (13) cannot exceed the values that are determined by the separated-atom energies, that is, 4, 16, and 36 for the states $|m| = 0, 1, 2$ in Fig. 1.

Turning now to systems with two electrons, since the united-atom energies can be determined only numerically, for such systems also at $R = 0$, we have to employ lower bound energies. In Refs. [5,9] rigorous and explicit $e_{\alpha,0}^{LB}$ are derived by the technique of "intermediate Hamiltonians" (or the "projection method"). These bounds are relatively sharp for charges Z not too small, but become
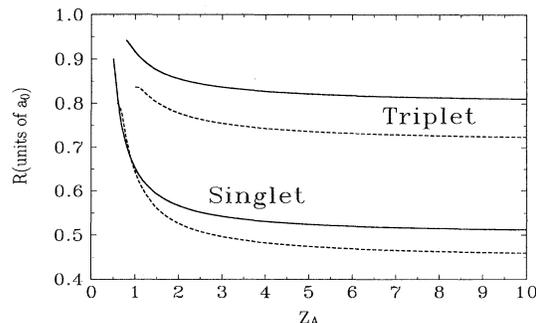
FIG. 2. Two-electron system: Lower bound R_e from united-atom lower-bound energies for $\eta = Z_B/Z_A = \frac{1}{1}$ (solid lines) or $\eta = \frac{1}{2}$ (short-dashed lines) and the lowest states in the singlet and triplet symmetry sector.

"trivial" (i.e., identical to values that result by neglecting the positive part v_{ee} of h; cf. [5 and 9]) for Z below a certain crossing point Z_c. In Fig. 2 lower bounds on R_e are displayed for singlet and triplet states with $\eta = 1$ and $\frac{1}{2}$. These lower-bound curves are computed by using a two-dimensional projection for the e_0^{LB} [Eq. (5) of Ref. [9]] and, due to the just-mentioned crossings, become constant [and equal to $18\eta/5(1+\eta)^2$ (singlet) or $64\eta/17(1+\eta)^2$ (triplet)] for Z_A smaller than the values shown in Fig. 2. For Z_A large, they converge—as expected—to the values $2\eta/(1+\eta)^2$ (singlet) or $16\eta/5(1+\eta)^2$ (triplet) corresponding to the trivial hydrogenic lower-bound energies. In addition, we tried "parabolic" e_0^{LB} [Eq. (8) of Ref. [9]] from a one-dimensional projection; although on a certain Z_A interval they yield larger R_e bounds, on the scale of Fig. 2, the difference would not be visible.

In the two-electron case, unfortunately only for symmetric systems and the ground state $X\,^1\Sigma_g^+$ are exact (numerical) R_e available for varying $Z = Z_A = Z_B$ (see Fig. 4 in Ref. [1]); the smallest $R_e = 1.263$ was observed at $Z = 1.605$. For the physically most important charges, our bounds yield $R_e \geq 0.657$ ($Z = 1$) or $R_e \geq 0.571$ ($Z = 2$) for all singlet states, and $R_e \geq 0.916$ ($Z = 1$) or $R_e \geq 0.856$ ($Z = 2$) for all triplet states. In comparison, the actual (numerical) values are $R_e = 1.401$ for $H_2(X\,^1\Sigma_g^+)$ (cf. Ref. [10]), $R_e = 1.328$ for $He_2^{2+}(X\,^1\Sigma_g^+)$ (cf. Ref. [1]), and $R_e = 1.868$ for $H_2(a\,^3\Sigma_g^+)$ (cf. Ref. [10]). If $\eta = \frac{1}{2}$ and $Z_A = 2$, we get $R_e \geq 0.531$ in the singlet and $R_e \geq 0.778$ in the triplet sector, compared with $R_e = 1.435$ and 4.47 for the lowest singlet or triplet states, respectively, of HeH^+ (cf. Ref. [11]). Better R_e bounds would result from sharper lower bounds on the united-atom energy; however, as can be verified by inserting the (almost) exact energies for the He isoelectronic series from Ref. [12], the maximal improvements achievable in this way are moderate (about 5% at $Z = 1$).

If the molecular system contains three or more electrons, the derivation of R_e bounds along the same lines is handicapped by the present lack of appropriate lower-bound energies $e_{\alpha,0}^{LB}$. The trivial hydrogenic $e_{\alpha,0}^{LB}(Z) = -NZ^2/2$ produces a uniform bound on R_e for all states of an N-electron molecule like the bound in Eq. (14) but with an additional factor N^{-1} on the right-hand side. For neutral systems (i.e., $Z = N$), in the limit $N \to \infty$, Thomas-Fermi theory leads to a lower-bound energy of the form

$$e_{\alpha,0}^{LB} = -(\tfrac{3}{2})^{1/3}N^{7/3} + O(N^2) .$$

This implies a lower bound on R_e that decreases as $N^{-1/3}$ for large N. Since there are no systematic studies of the N dependence of equilibrium configurations, the question of whether or not the shrinking of the lower bound with $N^{-1/3}$ is the correct asymptotic behavior for a Schrödinger molecule [modeled by the Hamiltonian (1) without relativistic or other corrections] cannot be answered here.

To summarize, the bound in Eq. (7) or its specialized versions (11)–(15) exclude small internuclear separations as candidates for molecular equilibrium positions. The quality of the obtainable R_e bounds depend on the entering lower-bound energies for the PEC's or united atoms. Comparison with exact R_e shows that for the lowest states, actual R_e values are within a factor 2 of the sharpest lower bound; possible improvements would require a sharper estimate (9) and may be difficult to achieve for the general case. A major advantage of the derived bounds is their uniformity in all states of the considered symmetry sector, so that they could find further applications in various other situations. Moreover, although we restricted our discussion here to diatomic molecules, a generalization of the bounds to linear symmetric configurations of polyatomic species is straightforward.

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