# Lower bounds on the ground-state energy and necessary conditions for the existence of bound states: The few-body problem

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We consider a positive diatomic molecule consisting of $N$ electrons and two nuclei and obtain some results that exhibit scaling properties of the adiabatic energy $E_{\rm ad}$—the ground-state energy with the nuclei fixed—under changes in the charges, and we obtain lower bounds on $E_{\rm ad}$. In particular, with the use of available numerical results for $E_{\rm ad}$ for a *single* electron in the Coulomb field of two fixed nuclei with charges $Z_A e$ and $Z_B e$, we show that composite bound states cannot be formed for $N=1$ and $Z_A+Z_B\geq 3$ nor for $N=2$ and $Z_A=Z_B\geq 3$, results not too far from the true lower limits.

## I. INTRODUCTION

The determination of a lower bound on the ground-state energy $E$ is much more difficult than the determination of an upper bound on $E$. The proof, where true, of the nonexistence of a bound state is more difficult still, and increases further when there is more than one particle involved. One useful approach[1] in an attempt to prove the nonexistence of a bound state for a certain systems is, as an intermediate step, to determine the lower bound on $E$ for a diatomic molecule in an adiabatic approximation in which the nuclei are fixed at a separation $r_{AB}$. The determination of a lower bound on the adiabatic energy $E_{\rm ad}(r_{AB})$ has an additional element of complexity in that one must choose an approach in which $E_{\rm ad}(r_{AB})$ becomes exact as $r_{AB}\to\infty$; we discuss this below. We will touch upon other methods, but our primary effort will involve the adiabatic approximation.

It will be useful to begin with a brief sketch of some concrete applications that have been made of the adiabatic approximation technique; we will thereby at the same time define the notation to be used. We consider a helium atom (with the nuclear mass $M_\alpha$ taken to be infinite) and a positron, and let the electron coordinates be $\mathbf{r}_1$ and $\mathbf{r}_2$ and the positron coordinate be $\mathbf{r}_3$. Then, in an obvious notation,

$$\begin{aligned} H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)&=(T_3+2e^2/r_3)\\ &\quad+(T_1+T_2-2e^2/r_1-2e^2/r_2\\ &\quad+e^2/r_{12}-e^2/r_{13}-e^2/r_{23})\\ &\equiv h(r_3)+\tilde{H}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_3)\ . \end{aligned} \tag{1.1}$$

(Here and later, $\tilde{H}$ denotes a Hamiltonian which arises on making an adiabatic approximation.) Since $\tilde{H}$ does not contain $T_3$, the positron coordinate $\mathbf{r}_3$ in $\tilde{H}$ can be taken to be a parameter—the positron is fixed. The determination of the ground-state energy $\tilde{E}(r_3)$ of $\tilde{H}(\mathbf{r}_1,\mathbf{r}_2;\mathbf{r}_3)$ is then a two-body problem, and even though it is a two-center problem, accurate numerical evaluations of $\tilde{E}(r_3)$ have been performed.[2,3] [The calculations were done within the context of the adiabatic approximation to the $H_2$ molecule. It makes no difference whether it is a proton or a positron ($e^+$) which is frozen.] We then have

$$H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\geq T_3+2e^2/r_3+\tilde{E}(r_3)\ . \tag{1.2}$$

(Mathematically, it follows immediately that $H=h+\tilde{H}\geq h+\min$ of $\tilde{H}$; physically, the result is understandable in that in the evaluation of $\tilde{E}$ the electrons have been allowed an arbitrary amount of time to adjust to each possible position of the $e^+$.) If we denote the ground-state energy of the helium atom by $E_{\rm He}$, it will then not be possible for the $e^+$ to be bound to a He atom if $T_3+V_{\rm eff}(r_3)$, with the effective potential defined by

$$V_{\rm eff}(r_3)\equiv 2e^2/r_3+\tilde{E}(r_3)-E_{\rm He}\ ,$$

cannot support a bound state. [Note that $\tilde{E}(r_3)\sim E_{\rm He}$ as $r_3\sim\infty$, so that $V(r_3)\sim 0$ as $r_3\sim\infty$.] The analysis of the three-body problem in a center of force for the existence of a bound state has thus been reduced to the *much* simpler analysis of a two-body (two-center of force) problem followed by a one-body problem. In the approximation considered (nonrelativistic theory, $M_\alpha=\infty$, no spin interactions), the above analysis[1] does indeed prove rigorously that the bound system ($e^+$+He) does not exist.

The adiabatic approach can in principle be applied to reduce the dimensionality of an $N$-body analysis, but in practice is limited to cases for which the lower-dimensional problem is solvable. Various extensions are also possible. Thus the approach as described above, with the $e^+$ initially frozen at a point $\mathbf{r}_3$, cannot prove the nonexistence of a bound state of an $e^+$ and a hydrogen atom, but the nonexistence of such a bound state can be proven by freezing the $e^+$ at a given value of $r_3$ rather than of $\mathbf{r}_3$; the intermediate analysis for this less crude approximation is more difficult, but doable. One can also allow for finite nuclear mass,[4] not particularly relevant for the $e^+$-He or $e^+$-H cases noted above, but significant for a problem such as $\mu^+$+H. The Hamiltonian $H_{\rm c.m.}$ in

 

the center of mass then includes a mass polarization term, but $H_{\text{c.m.}}$ can be bounded from below by a Hamiltonian of the same form as that for which the nuclear mass is infinite.[4]

Some formal results have been obtained relating the number of electrons $N$ and the atomic numbers $Z_A$ and $Z_B$ of two nuclei which can form a diatomic molecule. It was shown[5] that there exists a critical value $Z_c(N)$ such that no such molecule can exist if $Z_A > Z_c$ and $Z_B > Z_c$, where $Z_c \sim 2N$ as $N \sim \infty$. This result is understandable intuitively, the repulsive nucleus-nucleus Coulomb potential dominating over the attractive potential generated by the presence of the electrons, and it is both surprising and disturbing that more concrete results—for example, specific values of $Z_c$ for $N$ fixed—have not been obtained. It must be understood, however, that the attempt made limited itself to purely analytic results, with numerical results (either for the problem itself or from related problems) not allowed.

A number of other results in this area have been obtained, but these are unrelated to the approaches discussed below, and will therefore only be noted. Thus one can obtain lower bounds on the energy of some one-body central potential problems by using the Sobolov inequality to bound the kinetic energy,[6] and one can obtain a lower bound on the ground-state energy $E$ of bulk matter by using a many-body extension[7] of the Sobolov inequality. (The bound is of the form $E \geq -CN$, with $N$ the number of particles in the system, and therefore provides a proof[7] of the stability of matter which is simpler than the original proof.[8]) One can also obtain concrete results on the maximum number of electrons which can be bound to a group of nuclei with total charge $Z$ to form a negative molecular ion.[9] A very good lower bound on the ground-state energy of some simple systems, such as the He atom, can be obtained by a projection operator approach.[10] Methods applicable to more complicated systems, such as the Li atom, and capable of proving the nonexistence of some bound states, have been provided by Hill.[11] Finally, we note that while upper bounds on the scattering length $A$ can often rather readily be obtained[12,13] by methods which are extensions of the Rayleigh-Ritz approach, lower bounds on $A$ are much more difficult to obtain; lower bounds can be obtained for some systems by using an approach based on the adiabatic approximation.[14,15]

## II. SYSTEMS CONTAINING TWO NUCLEI AND ONE OR TWO ELECTRONS

### A. The one-electron case: Some scaling properties

Our three-body system consists of two particles, with charge and mass $Z_A e, m_A$ and $Z_B e, m_B$, respectively, and a particle with charge $-Z_1 e$ and mass $m_1$. The prototype problem is that of two nuclei and an electron. With $\mathbf{Z}$ representing $(Z_A, Z_B, -Z_1)$ and $\mathbf{m}$ representing $(m_A, m_B, m_1)$, we characterize the system by $(Z_A, m_A; Z_B, m_B; -Z_1, m_1)$, or, more simply, by $(\mathbf{Z}, \mathbf{m})$. The Hamiltonian is

$$H(\mathbf{Z},\mathbf{m}) = T - \frac{Z_A Z_1 e^2}{r_{A1}} - \frac{Z_B Z_1 e^2}{r_{B1}} + \frac{Z_A Z_B e^2}{r_{AB}} , \tag{2.1}$$

$$T \equiv T_A + T_B + T_1, \quad T_i \equiv -(\hbar^2/2m_i)\nabla_i^2 . \tag{2.2}$$

We denote the ground-state energy of the three-body system by $E(\mathbf{Z},\mathbf{m})$. Without loss of generality we can assume that

$$Z_A^2 \mu_{A1} \geq Z_B^2 \mu_{B1} ,$$

where

$$\mu_{ij} \equiv m_i m_j/(m_i + m_j) \tag{2.3}$$

is a reduced mass. The deepest continuum threshold $E_{\text{thr}}$ is then the ground-state energy of the $Z_A, m_Z$ and $Z_1, m_1$ pair, that is,

$$E_{\text{thr}} = -\frac{Z_A^2 Z_1^2 \mu_{A1} e^4}{2\hbar^2} .$$

To avoid having an infinite number of three-body bound states, we assume that $Z_A - Z_1 \geq 0$. Since a three-body bound state exists only if $E(\mathbf{Z},\mathbf{m})$ lies below $E_{\text{thr}}$, we define a new Hamiltonian $H^*(\mathbf{Z},\mathbf{m})$ with $E_{\text{thr}}$ as the zero-energy reference level, so that

$$H^*(\mathbf{Z},\mathbf{m}) \equiv H(\mathbf{Z},\mathbf{m}) - E_{\text{thr}} . \tag{2.4}$$

We let $\rho$ represent $(\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_1)$. If $H^*(\mathbf{Z},\mathbf{m})$ is nonnegative, that is, if

$$\langle \phi | H^*(\mathbf{Z},\mathbf{m}) | \phi \rangle \geq 0 \tag{2.5}$$

for every square integrable function $\phi(\rho)$, the system has no three-body bound state. A number of consequences follow from the assumption that (2.5) is valid.

(i) Replace $Z_A$ by $\lambda Z_A$, where here and later $\lambda \geq 1$. With $\hbar = e = 1$, $H^*(\mathbf{Z},\mathbf{m})$ is replaced by

$$H^*(\lambda Z_A) = T - \frac{\lambda Z_A Z_1}{r_{A1}} - \frac{Z_B Z_1}{r_{B1}} + \frac{\lambda Z_A Z_B}{r_{AB}} + \frac{1}{2}\lambda^2 Z_A^2 Z_1^2 \mu_{A1} .$$

[Here and later, the argument of the altered $H^*$ will indicate which of the parameter(s) has been changed.] Changing variables from $\rho$ to $\rho/\lambda$, we obtain

$$H^*(\lambda Z_A) = \lambda^2 H^*(\mathbf{Z},\mathbf{m}) + \lambda(\lambda - 1)(Z_B Z_1 / r_{B1}) \geq 0 .$$

In other words, the system with $Z_A$ replaced by $\lambda Z_A$ will not have a three-body bound state if the original system did not.

(ii) If $Z_A$ and $Z_B$ are replaced by $\lambda Z_A$ and $\lambda Z_B$, respectively, $H^*(\mathbf{Z},\mathbf{m})$ is replaced by $H^*(\lambda Z_A, \lambda Z_B)$. Under $\rho \to \rho/\lambda$, we find

$$H^*(\lambda Z_A, \lambda Z_B) = \lambda^2 H^*(\mathbf{Z},\mathbf{m}) + \lambda^2(\lambda - 1)(Z_A Z_B / r_{AB}) \geq 0 .$$

Again, the change does not generate a three-body bound state if there was no such bound state to begin with.

(iii) A similar result holds for the change $Z_1 \to Z_1/\lambda$. Under $\rho \to \lambda\rho$, we find

$$H^*(Z_1/\lambda)$$
$$=(1/\lambda^2)[H^*(\mathbf{Z},\mathbf{m})+(\lambda-1)(Z_AZ_B/r_{AB})]\geq 0 .$$

(In the Appendix we attempt to provide some physical insight into the above results.)

The results just obtained can be summarized as follows. Assume that the system defined by $(\mathbf{Z},\mathbf{m})$ has no three-body bound states and that the $A-1$ pair is more deeply bound than the $B-1$ pair. Then there will be no three-body bound states for a system for which (i) $Z_A$ is increased, (ii) $Z_A$ and $Z_B$ are increased by the same factor, and/or (iii) $Z_1$ is decreased.

Apart from some very special cases—for example, the absence of a bound state of tritium, an $e^+$ and $e^-$ guarantees, using (i), the absence of a bound state of $He^3$, an $e^+$ and $e^-$—results (i), (ii) and (iii) have little immediate applicability, since they were obtained under the assumption that the masses are held fixed, while a change in charge normally implies a change in mass.

As will be seen shortly, much more useful results can be obtained in the adiabatic approximation. Results (i), (ii), and (iii) are also valid in that approximation, and that is the context in which we first obtained them, but the derivations are simpler—and the results stronger—if one considers the original Schrödinger equation, as was pointed out by Robinson.[16]

### B. The one-electron case: some further general properties and some applications

We can deduce three additional simple scaling properties which allow changes in the nuclear masses as the nuclear charges are changed—essential in our approach to the proof of the nonexistence of certain bound states—if we make the adiabatic approximation and certain assumptions.

(iv) Assume that $m_A \gg m_B$ and $m_A \gg m_1$. Particle $A$ can then be taken to be fixed, and $T_A$ can be set equal to zero. The fact that $m_A$ increases with $Z_A$ is then irrelevant, and property (i) becomes applicable to some real systems.

(v) Consider a system for which the effective potential $V_{\text{eff}}(r_{AB})$, with particles $A$ and $B$ held fixed at a separation $r_{AB}$, is positive for all $r_{AB}$. Let $T_{AB}$ be the kinetic energy of relative motion of particles $A$ and $B$. It is then obvious that the Hamiltonian $T_{AB}(r_{AB})+V_{\text{eff}}(r_{AB})$ cannot support a bound state. With the superscript one on $\tilde{E}^{(1)}$ indicating that the system contains one electron, let $\tilde{E}^{(1)}(r_{AB};Z_A,Z_B)$ be the ground-state energy for an electron in the field of the two fixed nuclei, that is, for the Hamiltonian

$$\tilde{H}(\mathbf{r}_1;r_{AB},Z_A,Z_B)=T_1-\frac{Z_Ae^2}{r_{A1}}-\frac{Z_Be^2}{r_{B1}} .$$

Under $Z_A\to\lambda Z_A$, $Z_B\to\lambda Z_B$, and $\rho\to\rho/\lambda$, where, as always, $\lambda\geq 1$, we find

$$\tilde{E}^{(1)}(r_{AB};\lambda Z_A,\lambda Z_B)=\lambda^2\tilde{E}^{(1)}(\lambda r_{AB};Z_A,Z_B) . \quad (2.6)$$

Using the monotonicity theorem of Leib and Simon,[17] namely, that $\tilde{E}^{(1)}$ increases monotonically with increasing $r_{AB}$—$\tilde{E}^{(1)}$ becomes less negative—we arrive at

$$\tilde{E}^{(1)}(r_{AB};\lambda Z_A,\lambda Z_B)\geq\lambda^2\tilde{E}^{(1)}(r_{AB};Z_A,Z_B) .$$

The effective potential is

$$V_{\text{eff}}(r_{AB};Z_A,Z_B)=\tilde{E}^{(1)}(r_{AB},Z_A,Z_B)+\frac{Z_AZ_B}{r_{AB}}-E_{\text{thr}} ,$$

where

$$E_{\text{thr}}=-\tfrac{1}{2}m_1Z_A^2 .$$

It follows that ($\hbar=e=1$)

$$\begin{aligned}V_{\text{eff}}(r_{AB};\lambda Z_A,\lambda Z_B)&=\tilde{E}^{(1)}(r_{AB};\lambda Z_A,\lambda Z_B)\\&\quad+\frac{\lambda^2Z_AZ_B}{r_{AB}}+\frac{m_1\lambda^2Z_A^2}{2}\\&\geq\lambda^2V_{\text{eff}}(r_{AB};Z_A,Z_B)\\&\geq V_{\text{eff}}(r_{AB};Z_A,Z_B) . \quad (2.7)\end{aligned}$$

This result proves that if $V_{\text{eff}}(r_{AB},Z_A,Z_B)\geq 0$, then $V_{\text{eff}}$ for the system with $Z_A$ and $Z_B$ increased by a factor $\lambda$ will also be non-negative, so that the system cannot support a bound state, independent of the nuclear masses associated with the charges $\lambda Z_A$ and $\lambda Z_B$.

(vi) Replacing the nuclear charge $Z_A$ by $\lambda Z_A$, we have

$$\begin{aligned}V_{\text{eff}}(r_{AB};\lambda Z_A,Z_B)&=\tilde{E}^{(1)}(r_{AB};\lambda Z_A,Z_B)\\&\quad+\lambda\frac{Z_AZ_B}{r_{AB}}+\frac{1}{2}m_1\lambda^2Z_A^2 .\end{aligned}$$

Since the energy in the adiabatic approximation satisfies

$$\tilde{E}^{(1)}(r_{AB};\lambda Z_A,Z_B)\geq\tilde{E}^{(1)}(r_{AB};\lambda Z_A,\lambda Z_B) ,$$

we obtain, on using Eq. (2.6),

$$\begin{aligned}V_{\text{eff}}(r_{AB};\lambda Z_A,Z_B)&\geq\lambda^2\left[\tilde{E}^{(1)}(\lambda r_{AB};Z_A,Z_B)\right.\\&\quad\left.+\frac{Z_AZ_B}{\lambda r_{AB}}+\frac{1}{2}m_1Z_A^2\right]\\&=\lambda^2V_{\text{eff}}(\lambda r_{AB};Z_A,Z_B) . \quad (2.8)\end{aligned}$$

It follows that if $V_{\text{eff}}(r_{AB};Z_A,Z_B)\geq 0$, the system with $Z_A$ replaced by $\lambda Z_A$ cannot support a bound state.

It should be emphasized that subject to the assumption that $m_A\gg m_1$ the results in (v) and (vi) are rigorous; the adiabatic approximation generates a lower bound on the energy, and its use does not vitiate the proof.

The nonexistence of bound states of some systems can be proved using (iv), (v), and (vi) and available numerical results for $\tilde{E}^{(1)}(r_{AB};Z_A,Z_B)$.

(a) The system $(p,e^+,e^-)$ is known to have no three-body bound states.[18] Since $m_p\gg m_e$, it then follows from (iv) that a system containing a nucleus with $Z_A>1$, an $e^+$ and $e^-$ will not have any three-body bound states either.

(b) Consider systems consisting of an $e^-$ and two nuclei. An $\alpha$ particle ($m_A=m_\alpha$, $Z_A=2$), a proton ($m_B=m_p$, $Z_B=1$), and an $e^-$ are known[1] to have no three-body bound states, since it follows from the data of Bates, Ledsham, and Stewart and Wind[19] that

$V_{\text{eff}}(r_{AB};Z_A=2,Z_B=1)\geq 0$. The properties (v) and (vi) then give, respectively,

$$V_{\text{eff}}(r_{AB};Z'_A=2\lambda,Z'_B=\lambda)\geq 0\ ,$$
$$V_{\text{eff}}(r_{AB};Z'_A=2\lambda,Z_B=1)\geq 0\ . \tag{2.9}$$

with available numerical results[19] for $\tilde{E}^{(1)}(r_{AB};Z_A=Z_B=1)$ for $H_2^+$, and with the use of Eq. (2.7), we find that

$$V_{\text{eff}}(r_{AB};Z'_A=2\lambda,Z'_B=2\lambda)\geq 0\ . \tag{2.10}$$

Noting that $\lambda$ need not be integral, we conclude from (2.9), (2.10), and property (vi) that a system with total nuclear charge $Z_A+Z_B\geq 3$ has no three-body bound states. Consider, for example, the case $Z_A\geq 2$, $Z_B=2$. We would start with $Z_A=2$ and $Z_B=2$ in Eq. (2.10) and use property (vi) to conclude that a system with $Z_A\geq 2$ and $Z_B=2$ has no bound states. We can proceed similarly for the case $Z_B\geq 3$.

### C. Two-electron systems

Let $\tilde{E}^{(N)}(r_{AB};Z_A,Z_B)$ be the ground-state energy for $N$ electrons in the field of nuclei of charges $Z_A$ and $Z_B$ fixed at a separation $r_{AB}$. Numerical data exist for $N=2$, $Z_A=Z_B=1$, and for $Z_A=2$, $Z_B=1$. The latter data can be and have been used to prove that a He atom and an $e^+$ cannot be bound.[1] [$\tilde{E}^{(2)}(r_{AB};Z_A=1,Z_B=1)$ is the same for an $\alpha$ and an $e^+$ fixed as for fixed $\alpha$ and $p$.] It is obviously much less demanding, however, where possible, to use data for two fixed nuclei and *one* electron rather than two electrons, and we will now prove the nonexistence of bound states for some two-electron systems using only one-electron data. (Ultimately one would, of course, want to consider diatomic molecules with more than two electrons; for a consideration of such systems in the adiabatic approximation, the use of adiabatic energy data involving fewer than the true number of electrons would normally be essential.) As above, we denote the one-electron data by $\tilde{E}^{(1)}(r_{AB};Z_A,Z_B)$. Since the $e^-$-$e^-$ interaction is repulsive, we have

$$\tilde{E}^{(2)}(r_{AB};Z_A,Z_B)\geq 2\tilde{E}^{(1)}(r_{AB};Z_A,Z_B)\ .$$

Using (2.6), we find for the effective potential between the nuclei, in the two-electron case, with $Z_A=Z_B=Z$,

$$V_{\text{eff}}^{(2)}(r_{AB};\lambda Z,\lambda Z)\geq\lambda^2\left[2\tilde{E}^{(1)}(\lambda r_{AB};Z,Z)+\frac{Z^2e^2}{r_{AB}}+\frac{Z^2e^2}{a_0}\right]\ .$$

Setting $Z=1$ and using the numerical data for $\tilde{E}^{(1)}(r_{AB};Z,Z)$,[19] one finds that

$$2\tilde{E}^{(1)}(3r_{AB};1,1)+\frac{e^2}{r_{AB}}+\frac{e^2}{a_0}\geq 0\ ,$$

and therefore that $V_{\text{eff}}^{(2)}\geq 0$ for $\lambda\geq 3$. In other words, two electrons cannot bind two bare Li nuclei, nor two bare Be nuclei, etc.

### D. Conclusion and discussion

In Table I, we summarize the results obtained in this paper, and some of the results obtained previously, for systems which cannot form composite bound states. There are two major shortcomings in the approaches we have discussed. (1) All of the results obtained were based on numerical calculations. It would be desirable to have some rigorous analytic proofs. (2) None of the methods discussed allows generalization to systems with more than two electrons, and even for two electrons results were obtained only for $Z_A=Z_B$.

With regard to (1), consider, for example, an attempt to prove analytically that $Z_A$, $Z_B$, and $e^-$ cannot form a bound state, and let us specialize to the case $Z_A=Z_B\equiv Z$. One might begin by using the adiabatic approximation and then use the necessary condition[20]

$$\max[L(\mathbf{r};E)]\geq 1\ , \tag{2.11}$$

where

$$L(\mathbf{r};E)\equiv\int G(\mathbf{r},\mathbf{r}';E)V_-(\mathbf{r}')\psi_t(\mathbf{r}')d\mathbf{r}'/\psi_t(\mathbf{r}) \tag{2.12}$$

to bound $\tilde{E}^{(1)}(r_{AB};Z,Z)$. One might expect

$$\psi_t(\mathbf{r})=e^{-Z|\mathbf{r}-\mathbf{r}_{AB}/2|/a_0}+e^{-Z|\mathbf{r}+\mathbf{r}_{AB}/2|/a_0} \tag{2.13}$$

to be a reasonably good trial function—it would probably give a fairly good estimate of the energy—especially for $r_{AB}$ large. Since the objective is to show that $Z$, $Z$, and $e^-$ cannot have an energy below the ground-state energy $-Z^2e^2/(2a_0)$ of $Z$ and $e^-$, we must prove, for

$$F(\mathbf{r};r_{AB},E)\equiv\int G(\mathbf{r};\mathbf{r}';E)V(\mathbf{r}';r_{AB})\psi_t(\mathbf{r}')d\mathbf{r}'/\psi_t(\mathbf{r})\ ,$$

where $G$ is given by

$$G(\mathbf{r},\mathbf{r}';E)=-\left[\frac{2m}{\hbar^2}\right]\frac{e^{-\kappa|\mathbf{r}-\mathbf{r}'|}}{4\pi|\mathbf{r}-\mathbf{r}'|}\quad(\leq 0)\ , \tag{2.14}$$

and

$$V(\mathbf{r}';r_{AB})=(-Ze^2)\left[\frac{1}{|\mathbf{r}'-\mathbf{r}_{AB}/2|}+\frac{1}{|\mathbf{r}'+\mathbf{r}_{AB}/2|}\right]\ ,$$

TABLE I. Some systems which have been shown to be incapable of forming composite bound states.

| System | Condition | Reference |
|---|---|---|
| $\alpha+p+e^-$ | | Reference 1 |
| $Z_A+Z_B+e^-$ | $Z_A+Z_B\geq 3$ | Present work |
| $p+e^++e^-$ | | Reference 17 |
| $Z_A+e^++e^-$ | $Z_A\geq 1$ | Present work |
| $\alpha+e^++e^-+e^-$ | | Reference 1 |
| $Z_A+Z_B+e^-+e^-$ | $Z_A=Z_B\geq 3$ | Present work |
| $\mu^\pm+e^-+e^+$ and $p+\mu^-+e^+$ | | Reference 4 |

that the maximum over $\mathbf{r}$ of $F(\mathbf{r};r_{AB},E)$ approaches 1 when $r_{AB}$ approaches $\infty$ so that the lower bound on the energy approaches the deepest continuum threshold

$$E_{\text{thr}}=-\tfrac{1}{2}Z^2e^2/a_0 \ .$$

However, consider $r_{AB}$ arbitrarily large but fixed, and choose $r \gg r_{AB}$. The dominant contribution to $F$ comes from $\mathbf{r}' \approx \mathbf{r}$, and we arrive at

$$F(\mathbf{r};r_{AB},E_{\text{thr}}) \approx 2 \int G(\mathbf{r},\mathbf{r}';E_{\text{thr}})(-Ze^2/r') \times e^{-Zr'/a_0} d^3r' / e^{-Zr/a_0} = 2 \ ;$$

$\psi_t$ as given by Eq. (2.13) is therefore useless. That $\psi_t$ of Eq. (2.13) is very wrong for $r \gg r_{AB}$ is clear, for the $e^-$ is then effectively in the field of a point charge of magnitude $2Z$. [For $E=-Z^2e^2/(2a_0)$, the wave function is then proportional to that of a $2s$ state for nuclear charge $2Z$, very different from the $\psi_t$ of Eq. (2.13).]

There would also seem to be great difficulties in an attempt to apply the projection operator technique to bound $\tilde{E}(r_{AB};Z,Z)$. This is a two-center problem, and there is no obvious choice of $\tilde{H}_0$ in the decomposition $\tilde{H}=\tilde{H}_0+H'$, where

$$\tilde{H}(\mathbf{r}_1;\mathbf{r}_{AB};Z,Z)=T_1+V(\mathbf{r}_1;\mathbf{r}_{AB}) \ .$$

We are free to choose $\tilde{H}_0$ but the projection operator technique for obtaining a lower bound on the energy demands that $H'$ be non-negative *everywhere*, a severe restriction.

With regard to (2), we note that there do not seem to be any simple scaling laws for $N \geq 2$, where $N$ is the number of electrons, except for all of the $Z$'s the same. Even then the scaling law is not on the original Hamiltonian $H$ nor even on $\tilde{H}$, but on the $\tilde{H}$ with the $e^-$-$e^-$ terms omitted. (Though that omission will weaken the necessary conditions for the existence of bound states, it does preserve the lower bound on $\tilde{E}^{(N)}$.) Furthermore, scaling laws are not, by themselves, necessarily useful; one often needs a monotonicity theorem, which has been proved only for $N=1$ and may well not be valid for $N>1$, *and* there is the severe restriction on the adiabatic energy, namely, that it must satisfy

$$\tilde{E}^{(N)}(r_{AB}=\infty,\lambda Z_A,Z_B)=E_{\text{thr}}^{(N)}(\lambda Z_A,Z_B) \ . \qquad (2.15)$$

[By definition $E_{\text{thr}}^{(N)}$—which in general is a function of both charges—is the ground-state energy of the system of $N$ electrons and two nuclei for the nuclei infinitely far apart. Since the adiabatic approximation leads to a lower bound on the ground-state energy, $\tilde{E}^{(N)}(r_{AB},\lambda Z_A,Z_B)$ cannot lie above $E_{\text{thr}}^{(N)}(\lambda Z_A,Z_B)$; if it were to lie below, one could not possibly prove the nonexistence of a bound state.] Thus, for $N=2$, $Z_A=Z_B$, and $r_{AB}\to\infty$, one electron is attached to each nucleus, the $e^-$-$e^-$ repulsion can be neglected, and the condition of $\tilde{E}^{(2)}$ just recorded is satisfied, but for $Z_A \geq Z_B+1$ both electrons will be attached to $Z_A$ for $r_{AB}\to\infty$ and the condition on $\tilde{E}^{(2)}$ is *not* satisfied, and it does not seem to be satisfied even for $Z_A=Z_B$ for $N>2$. [Parenthetically, we note that $\tilde{E}^{(1)}$ is *not* monotonic for the system consisting of a proton, an electron, and an antiproton. Thus we have $E_{\text{thr}}=-\frac{1}{2}e^2/(a_0)$, and a polarization energy $E_{\text{pol}}=-\frac{1}{2}\alpha e^2/r_{AB}^4$ for large $r_{AB}$, where $\alpha=\frac{9}{2}a_0^3$ is the polarizability of the hydrogen atom. The adiabatic energy vanishes for $r_{AB}=0$ and is equal to $E_{\text{thr}}$ at $r_{AB}=\infty$, while for $r_{AB}$ very large it is equal to $E_{\text{thr}}+E_{\text{pol}}$, below its values at $r_{AB}=0$ and $r_{AB}=\infty$.] For $N>2$ there is, of course, the additional problem of having to satisfy the Pauli principle.

While the adiabatic approximation technique has the advantage of reducing the problem to a sequential pair of lower-dimensional problems, it has the disadvantage, noted just above, of requiring Eq. (2.15) to be satisfied. One might therefore consider other approaches. Thus, for example, for $N=1$ the necessary condition defined by (2.11) and (2.12) requires the use of the six-dimensional free Green's function—this might be reduced somewhat by using the azimuthal symmetry of the problem with respect to the axis joining the two nuclei—but the question of the validity of Eq. (2.15) does not arise.

*Note added in proof.* We had not considered the possibility that $Z_B<1$. Though not of immediate physical interest, the case is of considerable conceptual interest, as pointed out to us by Professor M. B. Ruskai. Thus, for $N=1$, assume that $r_{AB}$ is large and that the electron is bound to particle $B$. Since, for $Z_B<1$, the net charge of the bound system is negative, the interaction between the bound system and particle $A$ is attractive. One of course expects the electron to be bound to $A$ rather than to $B$ for $r_{AB}$ large, but the rigorous proofs for the nonexistence of composite bound states, for $Z_A$ arbitrarily large, depend explicitly on the assumption that the interaction is repulsive for large $r_{AB}$, whether the electron is attached to $A$ or $B$. That no bound state exists for $Z_B<1$ does not seem to follow from our results. We note without proof that it is not necessary to invoke the monotonicity theorem to prove properties (v) and (vi); one can simply use scaling.

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## APPENDIX: A VERY ROUGH ESTIMATE OF THE CHARGE AND MASS PARAMETERS FOR WHICH A SYSTEM IS JUST BOUND

We seek conditions on the parameters $\mathbf{Z}$ and $\mathbf{m}$ of a three-body system such that the system is just bound; we here abandon any pretense of rigor. The wave function for the bound-state system may then be significant only for $r_{BA}$ and $r_{B1}$ large compared to $r_{A1}$; a characteristic value of $r_{A1}$ is $\hbar^2/(\mu_{A1}Z_AZ_1e^2)\equiv\bar{a}_1$, the Bohr radius for the $A$-1 pair in its ground state. We can therefore hope to approximate $r_{B1}$ by $r_{BA}$. Further, the dominant interaction between $B$ and the $A-1$ pair may be given, for the values $r \gg \bar{a}_0$ under consideration, by

$$V_{\text{eff}}(r) \approx \frac{(Z_A-Z_1)Z_Be^2}{r}-\frac{1}{2}\alpha\frac{(Z_Be)^2}{r^4} \equiv V_C(r)+V_{\text{pol}}(r) \ ,$$

where, in this appendix and only in this appendix we write $r$ for $r_{BA}$, where by an earlier assumption $Z_A - Z_1 \geq 0$, and where $V_C$ is the Coulomb potential, $V_{\text{pol}}$ is the polarization potential, and $\alpha$ is the static electric dipole polarizability of the $A$-1 pair in its ground state. $\alpha$ is given by

$$\alpha = \frac{9}{2}\left[\frac{\hbar^2}{\mu_{A1}e^2}\right]^3 \frac{1}{Z_A^4 Z_1^4}\left[\frac{Z_1 m_A + Z_A m_1}{m_1 + m_A}\right]^2 .$$

Let $\mu$ be the reduced mass of the $B$-($A$-1) system, that is,

$$\mu = \frac{m_B(m_A + m_1)}{m_B + m_A + m_1} . \tag{A1}$$

The question as to whether or not $H(\mathbf{Z},\mathbf{m})$ can support a three-body bound state is then reduced to the question of whether or not the one-body Hamiltonian

$$h(\mathbf{r}) \equiv t + V_{\text{eff}}(r) \tag{A2}$$

can support a bound state, where

$$t = -(\hbar^2/2\mu)\nabla^2 . \tag{A3}$$

We will return to this question shortly, after having made some scaling studies. Let us first assume that $H^*(\mathbf{Z},\mathbf{m}) \geq 0$. If the one-body approximation is a good one, it can then be expected that

$$h(\mathbf{r}) \geq 0 . \tag{A4}$$

[Note that $h(\mathbf{r})$ is the one-body equivalent of $H^*(\mathbf{Z},\mathbf{m})$ in Eq. (2.4), *not* of $H(\mathbf{Z},\mathbf{m})$.] We will now determine whether the scaling laws for the original problem are valid for what one can hope is an approximately equivalent one-body problem, at least for $m_A \gg m_1$. For particle-1 an electron and for $m_A \gg m_e$, $h(\mathbf{r})$ reduces to

$$h(\mathbf{r}) = -\frac{\hbar^2}{2m_e}\nabla^2 + \frac{(Z_A - 1)Z_B e^2}{r} - \frac{CZ_B^2}{m_e^3 Z_A^4}\frac{1}{r^4} \tag{A5}$$

for $r$ rather large compared to $a_0/Z_A$, where

$$C \equiv \tfrac{9}{4}(\hbar^6/e^4) .$$

Under $Z_A \to \lambda Z_A$, one can see by inspection that $h(\lambda Z_A) \geq 0$, so that we obtain (i); the proof does not consider the change $\mathbf{r} \to \mathbf{r}/\lambda$. Similarly we obtain properties (ii) and (iii) from this one-body Hamiltonian; here we do need to consider that change. The fact that $h(\mathbf{r})$ has the same scaling properties as $H^*$ slightly increases our faith in the use of $h(\mathbf{r})$.

The critical values for the nuclear charges can also be estimated from a study of $h(\mathbf{r})$. The monotonicity theorem[17,21] provides a simple lower bound on the adiabatic ground-state energy for all $r_{AB}$. If, for simplicity, we take particle-1 to be an electron and choose $Z_A = Z_B \equiv Z$ for the nuclear charge, we have

$$\tilde{E}(r_{AB};Z,Z) \geq -\frac{(2Z)^2 e^2}{2a_0} .$$

The lower bound for $V_{\text{eff}}$ is then given as

$$V_{\text{eff}}(r_{AB};Z,Z) \geq \frac{Z^2 e^2}{r_{AB}} - \frac{2Z^2 e^2}{a_0} + \frac{Z^2 e^2}{2a_0} .$$

The effective potential $V_{\text{eff}}$ is then non-negative for $r_{AB} \leq \frac{2}{3}a_0$. On the other hand, it follows from the $V_{\text{eff}}$ of Eq. (A5) that $V_{\text{eff}}(r_{AB}) \geq 0$ for $r_{AB} \geq \frac{2}{3}a_0$ if $Z$ satisfies

$$32Z^4 - 32Z^3 - 243 \geq 0 ,$$

which gives $Z \geq 2.0$, to be compared with the more accurate numerical value $Z \geq 1.4$. (Analogous results can readily be obtained for arbitrary $\mathbf{Z}$ and $\mathbf{m}$.) It must be stressed that the estimate $Z \geq 2.0$ is indeed an estimate, not a rigorous bound. If, for example, one includes the $r^{-6}$ terms in $V_{\text{eff}}$, terms originating in the static electric quadrupole polarizability and in nonadiabatic effects, the estimate becomes $Z \geq 1.1$, below the more accurate numerical value.

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