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Atomic and Molecular Negative Ions

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An upper bound is given for the maximum number, N_c, of negative particles (fermions or bosons or a mixture of both) of charge $-e$ that can be bound to an atomic nucleus of charge $+ze$. If z is integral then $N_c \leq 2z$. In particular, this is the first proof that H^{--} is not stable. For a molecule, $N_c \leq 2Z+K-1$, where K is the number of atoms in the molecule and Z is the total nuclear charge.

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One of the striking, nonperiodic facts about the periodic table is that the maximum number of electrons, N_c, that can be bound to a nucleus of charge z is never more than $z+1$. Recently, several authors[1-8] have attempted to find bounds on N_c; one of the strongest results so far[8] (for fermions) is that $\lim_{z\to\infty} N_c/z=1$. For *bosons*,[5] however, $N_c > 1.2z$ for large z. Thus, the value of N_c is very dependent on the statistics of the bound particles.

The purpose of this note is to announce a theorem about N_c, the full details of which will appear elsewhere.[9] The theorem applies to *any mixture* of bound particles, with possibly different statistics, masses, and charges (as long as they are all negative), and even with possibly different magnetic fields acting on the various particles. (Naturally, symmetry requires that particles of the same type have the same mass, etc.) The theorem also applies to a molecule. The usual approximation that the nuclei be fixed (or infinitely massive) is important, but if they are not fixed a weaker theorem holds. The same theorems hold in the Hartree-Fock (restricted or unrestricted) and Hartree approximations to the ground-state energy.[9]

Suppose that we have a molecule with K nuclei of charges $z_1,\ldots,z_K>0$ (units are used in which the electron charge is unity) located at fixed, distinct positions $\vec{R}_1,\ldots,\vec{R}_K$. The electric potential of these nuclei is

$$V(\vec{x}) = \sum_{j=1}^{K} z_j |\vec{x}-\vec{R}_j|^{-1}. \tag{1}$$

Let there be N negative particles with masses $m_1,\ldots,m_N$ and charges $-q_1,\ldots,-q_N<0$ (in the usual case each $q_i=1$) and let each be subject to (possibly different) magnetic fields $\vec{A}_1(\vec{x}),\ldots,\vec{A}_N(\vec{x})$. (The generality of allowing nonintegral nuclear and negative particle charges may have some physical relevance because, as pointed out to me by W. Thirring, particles in solids such as semiconductors may have nonintegral effective charges due to dielectric effects.) The Hamiltonian is

$$H_N = \sum_{j=1}^{N} \{T_j - q_j V(\vec{x}_j)\} + \sum_{1\leq i<j\leq N} q_i q_j |\vec{x}_i - \vec{x}_j|^{-1}. \tag{2}$$

Here, T_j is the kinetic energy operator for the jth particle and it is one of the following (possibly different for different j) two types (nonrelativistic or relativistic):

$$T_j = [\vec{p}_j - q_j \vec{A}_j(\vec{x})/c]^2/2m_j, \tag{3}$$

$$T_j = \{[\vec{p}_j c - q_j \vec{A}_j(\vec{x})]^2 + m_j^2 c^4\}^{1/2} - m_j c^2. \tag{4}$$

Let q denote the maximum of the q_j, let $Q=\sum_{j=1}^N q_j$ be the total negative charge, and let $Z=\sum_{j=1}^K z_j$ be the total nuclear charge. Let E_N denote the ground-state energy of H_N [$\equiv \inf \operatorname{spec}(H_N)$].

Theorem 1.—If the above system is bound (meaning that E_N is an eigenvalue of H_N) then, necessarily,

$$Q < 2Z + qK. \tag{5}$$

In the atomic case ($K=1$) this can be strengthened to

$$Q < 2Z + \sum_{j=1}^N q_j^2/Q. \tag{6}$$

The strict inequality in Eqs. (5) and (6) is important; in the atomic case with $q=1$ and z integral, Eq. (5) implies

$$N_c \leq 2z. \tag{7}$$

For a hydrogen atom ($z=1$), Eq. (7) implies that $N_c=2$ (since it is known that two electrons can, in fact, be bound). H^{--} is *not* stable. This result had not been proved before, although there exist partial results in this direction.[6]

Although Eq. (7) is far from optimal when z is large [in view of the $N\approx z+O(1)$ conjecture], it is the strongest explicit estimate obtained so far and it is of the right order of magnitude for bosons (recalling the $N_c > 1.2z$ result[5]).

The theorem holds even if the nuclei are not points, but are spherical charge distributions, i.e., $|\vec{x}-\vec{R}|^{-1}$ is replaced by $\int d\mu(\vec{y})|\vec{y}-\vec{x}-\vec{R}|^{-1}$ in Eq. (1), where μ is any positive, spherical measure of unit total charge.

If the nuclear coordinates, $\vec{R}_j$, are dynamical instead of fixed, a weaker theorem holds. Let $\tilde{H}_N = H_N + T_{\text{nucl}} + U(\vec{R})$, where T_{nucl} is the nuclear kinetic energy [consisting of terms of the form in Eqs. (3) and (4)] and $U(\vec{R})$ is a potential depending on the nuclear coordinates. Let $\tilde{E}_N$ be the ground-state energy of $\tilde{H}_N$ and let $\tilde{E}_{N,j}{}^\infty$ be the ground-state energy when the nuclear masses are infinite (i.e., T_{nucl} is omitted) and the negative particle j is removed. If $\tilde{E}_{N,j}$ is the ground-state energy when particle j is removed, but T_{nucl} is retained, it is easy to see that $\tilde{E}_{N,j} \geq \tilde{E}_N$ and $\tilde{E}_{N,j} \geq \tilde{E}_{N,j}{}^\infty$. The theorem for dynamical nuclei, which assumes an additional inequality, is the following.

Theorem 2.—If the N-particle system is bound and if, in addition, $\tilde{E}_N \leq \tilde{E}_{N,j}{}^\infty$ for all $j=1,\ldots,N$, then Eq. (5) [respectively Eq. (6) for $K=1$] holds.

The proof of the theorems is simple enough to be given in an elementary quantum mechanics course—at least in the atomic case with fixed nucleus and with $T_j = p_j^2/2m_j$ (all j). The proof (ignoring some technical fine points) in this atomic case is the following: Take $\hbar^2/2m=1$ and $\vec{R}=0$. Pick some j and write $H_N = H_{N,j} + h_j$, where $H_{N,j}$ is the Hamiltonian for the remaining $N-1$ particles and

$$h_j = T_j - q_j z|\vec{x}_j|^{-1} + \sum_{k\neq j} |\vec{x}_j - \vec{x}_k|^{-1} q_j q_k. \tag{8}$$

Assume that the system is bound and let ψ be the ground state (which is real). Multiply the Schrödinger equation, $H_N\psi = E_N\psi$, by $|\vec{x}_j|\psi$ and integrate over all N variables. Let X_j denote all the $N-1$ variables other than $\vec{x}_j$. For the $H_{N,j}$ term, do the $d^{3(N-1)}X_j$ integration first; by the variational principle, the X_j integral is, for each fixed $\vec{x}_j$, not less than $E_{N,j}$ ($\equiv$ the ground-state energy of $H_{N,j}$) times the same integral without $H_{N,j}$. This inequality is preserved after the $\vec{x}_j$ integration since $|\vec{x}_j|$ is a positive weight. Thus

$$\langle |\vec{x}_j|\psi|H_{N,j}|\psi\rangle \geq E_{N,j}\langle|\vec{x}_j|\psi|\psi\rangle. \tag{9}$$

Recalling the easily proved fact that $E_N \leq E_{N,j}$, we have

$$\langle|\vec{x}_j|\psi|h_j|\psi\rangle \leq 0. \tag{10}$$

The claim is that Eq. (10) cannot hold for all j if condition (6) is violated.

First, the term $t_j = \langle|\vec{x}_j|\psi|p_j^2|\psi\rangle$ is positive. To see this, do the $\vec{x}_j$ integration first and note that it then suffices to prove the following for any function, f, of one variable:

$$t = -\int|\vec{x}|f(\vec{x})\nabla^2 f(\vec{x})d^3x > 0. \tag{11}$$

Write $g(\vec{x}) = |\vec{x}|f(\vec{x})$ and integrate by parts:

$$t = \int \nabla g(\vec{x})\cdot\{|\vec{x}|^{-1}\nabla g(\vec{x}) + g(\vec{x})\nabla|\vec{x}|^{-1}\}d^3x$$

$$= \int\{|\nabla g(\vec{x})|^2|\vec{x}|^{-1} - \tfrac{1}{2}g(\vec{x})^2\nabla^2|\vec{x}|^{-1}\}d^3x > 0$$

since $\nabla^2|\vec{x}|^{-1} \leq 0$. (The fact that $g\nabla g = \nabla g^2/2$, together with another integration by parts, was used for the second term.)

The second term in h_j is easy:

$$A_j \equiv q_j\langle|\vec{x}_j|\psi|V(\vec{x}_j)|\psi\rangle = q_j z\langle\psi|\psi\rangle = q_j z,$$

with the assumption that ψ is normalized.

The third term is

$$R_j \equiv \int\psi(X)^2|\vec{x}_j|\sum_{k\neq j} q_j q_k|\vec{x}_j - \vec{x}_k|^{-1} d^{3N}X,$$

where X denotes all the N variables.

If there is binding then Eq. (10) holds for all j and hence, summing over j and using $t_j > 0$, we have that $A \equiv \sum_j A_j > \sum_j R_j \equiv R$. On the one hand,

$A = z\sum_j q_j = zQ$. On the other hand,

$$R = \tfrac{1}{2}\int \psi(X)^2 \sum\sum_{k\neq j} q_j q_k |\vec{x}_j - \vec{x}_k|^{-1}(|\vec{x}_j| + |\vec{x}_k|)\, d^{3N}X.$$

But $|\vec{x}_j| + |\vec{x}_k| \geq |\vec{x}_j - \vec{x}_k|$ (triangle inequality), so that

$$R \geq \tfrac{1}{2}\sum\sum_{k\neq j} q_j q_k = \tfrac{1}{2}Q^2 - \tfrac{1}{2}\sum_j q_j^2.$$

Hence, binding implies that

$$Q^2 - \sum_j q_j^2 < 2zQ,$$

which is precisely Eq. (6). Q.E.D.

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