# Covalent Molecular Binding in a Susy Background

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**Abstract**

The Pauli Exclusion principle plays an essential role in the structure of the current universe. However, in an exactly supersymmetric (susy) universe, the degeneracy of bosons and fermions plus the ability of fermions to convert in pairs to bosons implies that the effects of the Pauli principle would be largely absent. Such a universe may eventually occur through vacuum decay from our current positive vacuum energy universe to the zero vacuum energy universe of exact susy. It has been shown that in such a susy universe ionic molecular binding does exist but homonuclear diatomic molecules are left unbound. In this paper we provide a first look at covalent binding in a susy background and compare the properties of the homonuclear bound states with those of the corresponding molecules in our universe. We find that covalent binding of diatomic molecules is very strong in an exact susy universe and the interatomic distances are in general much smaller than in the broken susy universe.

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# I   Introduction

String theory suggests that our current universe with a positive vacuum energy will in the future make transitions to other minima of the effective potential. For a review see ref. [1] .This prediction acquires added cogency from the essentially established fact that such a transition was made from an inflationary era in the very early universe to our current universe with a small but non-zero cosmological constant. Among the possibly numerous local minima of string theory [2] are some with exact susy and zero vacuum energy such as in

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the five original superstrings. If the universe falls into one of these minima it might remain there indefinitely since there are no vacuum fluctuations in these vacua. It is therefore of potential physics interest to contemplate the properties of bulk susy matter. We envision a scenario similar to that of chain inflation [3] in which a susy ground state of the universe with zero vacuum energy seems plausible. However, as exemplified in this paper, in bulk matter the energy advantage of a system of bosons relative to a system of fermions with similar interactions far outweighs the vacuum energy advantage. Even apart from the possibility of a phase transition to exact susy, the calculation described in this paper could serve in an academic way to elucidate the significance of the Pauli principle in our universe.

We assume that our current universe has a broken susy with masses of the bosonic quarks and leptons at the hundred GeV to one TeV scale. This may be confirmed in the near future at the Large Hadron Collider (LHC). Since, as in Lagrangian Higgs models, the number of degrees of freedom is preserved in a transition between local minima, we would expect that any future susy universe would have degenerate fermionic and scalar electrons, neutrinos, quarks, nucleons etc. In graphs and tables we assume for definiteness that the common mass of these susy multiplets is equal to that of the corresponding standard model particles in our broken susy universe where the electron has mass $m = 0.511$ MeV. Other assumptions for the common mass could be investigated since we give simple expressions for the Hamiltonian expectation value of the homonuclear diatomic molecules as a function of the common electron/selectron mass in a simple variational calculation with two parameters.

In the following section II we present this calculation. We use a generalization of the Heitler-London (HL) wave function [4] first employed in the case of the hydrogen molecule, $H_2$. A generalization to heavier elements is complicated in our universe due to the Pauli principle. However, in a susy universe where electrons freely convert in pairs to bosonic electrons, the generalization of the HL wave function could provide comparable accuracy for the binding of the heavier elements of moderate atomic number as the original calculation gave for $H_2$. In the summary and discussion presented in section III we discuss several obvious improvements of the variational wave function which could be made to improve the accuracy of the binding energies. At present, however, it is not our intention to perform a state-of-the-art molecular physics calculation but to present some simple results which are unlikely to be qualitatively invalidated by later refinements.

Certain integrals which occur in the calculation are given analytically in appendix A and a method for calculating combinatoric factors is described in appendix B.

## II  Variational Wave Function for Diatomic Molecules

For a multi-electron system of $N$ electrons in the presence of a nucleus of charge $Z$ the electronic Hamiltonian, including electron-electron repulsion, is

$$H = -\frac{1}{2m} \sum_{i=1}^{N} \nabla_i^2 - Ze^2 \sum_{i=1}^{N} \frac{1}{r_i} + e^2 \sum_{i<j}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad . \tag{2.1}$$

In a recent paper [5] a variational wave function for a susy atomic ion of atomic number $Z$ with $N$ susy electrons was given in the form:

$$\psi = \prod_{i=1}^{N} u(\vec{r}_i) \tag{2.2}$$

with

$$u(\vec{r}_i) = \sqrt{\frac{Z_s^3}{\pi}} e^{-Z_s|\vec{r}_i|} \quad . \tag{2.3}$$

This corresponds to putting all $N$ electrons into a $1s$ wave function which is a poor approximation for $N > 2$ in our world due to the Pauli principle. However, in a susy world it could be a quite adequate approximation to the ground state wave function since fermionic electrons in excited states would convert in pairs to bosonic electrons (selectrons) which would then drop into the $1s$ ground state via photon emission. To account for the mutual repulsion between electrons, $Z_s$ in eq. 2.3 is treated as a variational parameter which minimizes the expectation value of the Hamiltonian by taking the value

$$Z_s = me^2(Z - \frac{5}{16}(N-1)) \quad . \tag{2.4}$$

Therefore the effective nuclear charge seen by an electron is reduced from $eZ$ to $eZ_{eff} = e(Z - (N-1)5/16)$ due to screening by other electrons. The radius of the atom is correspondingly increased by a factor of $Z/Z_{eff}$. In treating the covalent binding of two such atoms we will use the wave functions of eq. 2.3 centered on two nuclei at $\pm\vec{R}$. We shall see that the value of $Z_s$ that minimizes the energy will differ slightly from eq. 2.4

The Bohr radius for hydrogen is

$$\frac{1}{me^2} = a_0 = 0.529 A^\circ \quad . \tag{2.5}$$

We work in a system of units where $\hbar = c = 1$ so

$$2R_\infty = \frac{1}{ma_0^2} = me^4 \tag{2.6}$$

$R_\infty$ being the Rydberg constant, 13.6 eV, and $e^2$ being the fine structure constant $1/137$. The variational estimate of the atomic energy is then

$$E(Z,N) = -R_\infty N Z_{eff}^2 = -R_\infty N(Z - 5(N-1)/16)^2 \quad . \tag{2.7}$$

For the neutral atom ($N = Z$), $Z_{eff} > 11Z/16 \propto Z$. Hence with increasing $Z$, the atoms become smaller as the radius decreases as $\sim 1/Z$ and the binding energy rapidly increases as $Z^2$. As discussed in section III, further refinements of the variational wave function are not expected to change these results qualitatively. From Eq. (2.7) we see that energy involved in subtracting or adding electrons to a neutral atom increases rapidly with $Z$. For example, the ionization energy of $K(Z = 19)$ is 105 eV, and the electron affinity of $Cl(Z = 17)$ is 146

eV. In contrast, the corresponding energies in our universe are of the order a few eVs, and do not depend strongly $Z$.

From 2.7 it is a simple matter to estimate the classical ionic binding energy by bringing two such atoms to a distance of twice the atomic radius, taking $l$ electrons from one atom and adding them to the other taking into account the consequent Coulomb attraction. In general the ionic binding is much greater in the susy system than in the standard model molecules. We find that the binding energy increases rapidly with increasing $\Delta Z = |Z_1 - Z_2|$. This is because it is energetically favorable for a low-Z atom to give up an electron or two to a high-Z atom since ionization energy and electron affinities increase rapidly with $Z$. However, the ionic binding energy is found to be negative (anti-bonding) for homonuclear molecules ($\Delta Z = 0$) in both the susy and standard model systems.

Covalent bonding is an intrinsically quantum mechanical effect where one or more electrons are simultaneously shared by two nuclei. In a susy system the lowest energy will be found by the totally symmetric wave function with at most two fermionic electrons.

Our approach is to follow the early quantum mechanical treatments of molecular bonding while discounting the effects of the Pauli principle. We consider a diatomic system of two atoms each having nuclear charge $Z$ and $N = Z$ electrons.

One might try the many electron generalization of the molecular orbital method [6] corresponding to the wave function

$$\Psi \propto \prod_{i=1}^{2N} \left( u(\vec{r}_i + \vec{R}) + u(\vec{r}_i - \vec{R}) \right) \quad . \tag{2.8}$$

Here $2R = D$ is the interatomic distance to be determined variationally. Although this gives a rough approximation to the $H_2$ molecule it would not be a serious candidate for a many-electron molecule in our universe due to the Pauli principle. In the susy case it becomes of interest to consider this wave function for larger $N$. The wave function 2.8 will be an exact solution in the absence of e-e interaction. However, for small $\Delta Z$ it does not work well since the wave function, when multiplied out, contains a preponderance of ionic configurations in which one atom has more electrons than the other. These are not favorable energetically because of electron-electron repulsion within the atom, and as noted above, lead to unstable ionic bonding for homonuclear molecules. Further, since the weights of these configurations do not depend on $R$, the total energy in the wave function of eq. 2.8 does not approach twice the energy of the isolated atoms given by eq. 2.7. In the actual state the electrons' motion will be correlated to keep them apart. Indeed, for moderate values of $Z$, the energy expectation value for the wave function eq 2.8 is found to be greater than that from the generalization given below of the Heitler-London wave function [4] which therefore provides a better approximation to the true wave function.

We consider, therefore, avariational wave function of the form:

$$\Psi = N_0(N) \left( \prod_{i=1}^{N} u(\vec{r}_i - \vec{R}) \right) \left( \prod_{j=N+1}^{2N} u(\vec{r}_j + \vec{R}) \right) + permutations(\vec{r}_i \leftrightarrow \vec{r}_j) \quad . \tag{2.9}$$

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Here $N_0(N)$ is a normalization constant. Note that there are equal number of electrons centered on each atom. The permutations make the wave function totally symmetric as appropriate to bosonic electrons. If there are (up to two) fermionic electrons in the system, they would also be expected to have a ground state in the totally symmetric state since other possibilities would be partially anti-bonding. We do not discuss excited states in the current paper nor do we consider possible mixing effects between states of differing number of fermionic electrons. In the presence of the other atom, $Z_s$ would be $R$ dependent and would be expected to approach that of the isolated atoms given by eq. 2.4 as $R \to \infty$. We treat $Z_s$ and $R$ as variational parameters to minimize the energy.

In the general case, the symmetrization of the wave function leads to a complex combinatorial problem involving a large number of terms each of which is a product of $2N$ $u$'s. These can be grouped into configurations with $N+m$ electrons in the wave function, $u = u(|\vec{r}-\vec{R}|)$, centered on the nucleus at $\vec{R}$ and $N - m$ electrons centered at $-\vec{R}$. The solution of this problem is given in Appendix B. Here we specialize to $m = 0$ which corresponds to the wave function of eq. 2.9. In this case there are $(2N)!/N!^2$ permutations, including the stated reference configuration where the first $N$ electrons are centered at $\vec{R}$ and the second $N$ electrons are centered at $-\vec{R}$. Among the permutations, the number of terms with $k$ interchanges is the square of the binomial coefficient

$$n(k) = \binom{N}{k}^2 \quad . \tag{2.10}$$

Note that

$$\sum_{k=0}^{N} n(k) = (2N)!/N!^2. \tag{2.11}$$

As a function of $Z_s$ and $R$ we minimize the expectation value of the Hamiltonian written as a sum of kinetic, electron-nucleus Coulomb terms, electron-electron correlation terms, and nucleus-nucleus repulsion term.

$$H_{kin} = -\frac{1}{2m} \sum_{i=1}^{2N} \nabla_i^2 \tag{2.12}$$

$$H_{Ze} = -Ze^2 \sum_{i=1}^{2N} \left( \frac{1}{|\vec{r}_i - \vec{R}|} + \frac{1}{|\vec{r}_i + \vec{R}|} \right) \tag{2.13}$$

$$H_{ee} = e^2 \sum_{i<j}^{2N} \frac{1}{|\vec{r}_i - \vec{r}_j|} \tag{2.14}$$

$$H_{nuc} = Z^2 e^2 / |2\vec{R}| \tag{2.15}$$

The corresponding expectation values are written in terms of one-body and two-body integrals, $A_i$, summarized in appendix A together with combinatoric factors discussed in appendix B. Each expectation value takes the form of a sum over $k$, the number of interchanges. The normalization of the wave function, for example, requires that

$$(N_0(N))^2 \binom{2N}{N} = \left( \sum_{k=0}^{N} n(k) A_0^{2k} \right)^{-1} \tag{2.16}$$

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The results are

$$< \Psi | H_{kin} | \Psi > = (N_0(N))^2 \binom{2N}{N} \frac{Z_s^2}{m} \sum_{k=0}^{N} n(k) \left( (N-k)A_0^{2k} + kA_1 A_0^{2k-1} \right) \qquad (2.17)$$

$$< \Psi | H_{Ze} | \Psi > = -2(N_0(N))^2 \binom{2N}{N} Z_s Z e^2 \sum_{k=0}^{N} n(k) \left( (N-k)(1+A_{2a})A_0^{2k} + kA_{2b}A_0^{2k-1} \right)$$
$$(2.18)$$

$$< \Psi | H_{ee} | \Psi > = (N_0(N))^2 \binom{2N}{N} Z_s e^2 \sum_{k=0}^{N} n(k) \left( A_{3c}A_0^{2k-2}k(2k-1) + 4k(N-k)A_{3b}A_0^{2k-1} \right.$$
$$\left. + A_0^{2k}(N-k)(I_3(N-k-1) + A_{3a}(N-k)) \right) \qquad . \qquad (2.19)$$

In the large $R$ limit

$$< \Psi | H | \Psi > \rightarrow N \left( Z_s^2/m - 2e^2 Z_s(Z - 5(N-1)/16) \right) \qquad (2.20)$$

This is a minimum at

$$Z_s = me^2(Z - 5(N-1)/16) = (Z - 5(N-1)/16)/a_0 \qquad (2.21)$$

with

$$< H > \rightarrow -2R_\infty N(Z - 5(N-1)/16)^2 \qquad . \qquad (2.22)$$

Thus at large separation the energy of the diatomic system approaches twice the energy of each isolated atom given in eq. 2.7. By examining the asymptotic forms for the integrals $A_i$ one can see that for large $R$ the asymptotic energy is generally approached exponentially.

At intermediate values of the separation we write

$$Z_s = (Z - 5(N-1)/16)(1+\delta)/a_0 \qquad . \qquad (2.23)$$

We vary $\delta$ and the interatomic separation $2R$ to minimize the energy. In figure 1 we show for $H_2$ the expectation value $< H >$ as a function of $R$ at the optimum value of $\delta$ for each $R$. In table 1 we give the results of the overall minimization for the eight lowest homonuclear diatomic molecules. We show for each molecule the minimum energy and equilibrium interatomic separation as well as the overall optimum value of $\delta$. We neglect the vibrational energy of the nuclei in the ground state so we do not distinguish between the minimum value of the Hamiltonian and the negative of the dissociation energy.
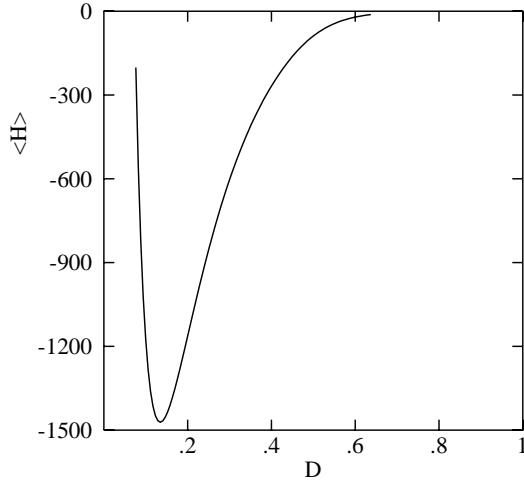
Figure 1: For the case of the $O_2$ molecule with bosonic constituents the graph plots the expectation value of the Hamiltonian in $eV$ as a function of the interatomic distance $D$ in $A°$. For each value of $D$, the $\delta$ parameter is chosen to minimize the energy.

| | $D$ $(A°)$ | $H_{min}(susy)$ | $\delta$ | $D(fermionic)$ | $B.E.(fermionic)$ |
|---|---|---|---|---|---|
| $H_2$ | 0.748 | -3.782 | 0.166 | 0.74 | 4.71 |
| $He_2$ | 0.454 | -27.15 | 0.208 | 2.97 | 0.0009 |
| $Li_2$ | 0.326 | -86.04 | 0.222 | 2.67 | 5.4 |
| $Be_2$ | 0.254 | -196.3 | 0.228 | - | - |
| $B_2$ | 0.208 | -374.0 | 0.231 | 1.59 | 3.0 |
| $C_2$ | 0.176 | -635.0 | 0.234 | 1.24 | 6.21 |
| $N_2$ | 0.153 | -995.6 | 0.235 | 1.10 | 9.76 |
| $O_2$ | 0.135 | -1471.6 | 0.237 | 1.21 | 5.12 |

Table 1: Binding properties of the eight lightest homonuclear diatomic molecules with totally symmetric electronic wave function as would be appropriate in the susy case. In the second column we give the interatomic distance ($D = 2R$) in angstroms. The corresponding minimum energy expectation value is given in $eV$ in the third column. The fourth column gives the $\delta$ parameter at the minimum. The fifth and sixth columns give the experimental [7] interatomic distance in angstroms and the experimental binding energy in $eV$ for the diatomic molecules of the current universe (fermionic constituents). Neglecting vibrational energy the experimental binding energy is the negative of the potential at the minimum.

# III    Discussion

We have studied the molecular properties of the first eight homonuclear diatomic molecules in a totally symmetric HL electronic ground state as would be appropriate in a susy background where fermionic and bosonic electrons are degenerate in mass. This wave function was used for $H_2$ by Wang [8] in the early days of quantum mechanics.

Our results for $H_2$ are in good agreement with those of that paper obtained in the days before computers. For instance our results from table 1 for the $H_2$ case can be compared with his interatomic distance of 0.76 $A°$, minimum energy of $-3.76$ eV, and $\delta$ parameter 0.166. The $H_2$ calculation, but not that for heavier molecules, is the same for bosonic as for fermionic electrons due to the absence of Pauli effects.

Our model calculation and that of Wang is 20% below the experimental binding energy of 4.71 eV. For the interatomic distance these calculations are good to about 1%. We can expect that similar accuracies would hold in the susy case for the diatomic molecules above $H_2$. The interatomic distances predicted in table 1 are somewhat less than twice the radii of the isolated atoms $3/(2Z_s)$.

In the case of the higher molecules, our calculation shows progressively smaller interatomic distances compared to the experimental values for the molecules with fermionic electrons which are all of order of $1A°$. The third column of table 1 shows the energy of diatomic molecule relative to the total energy of two isolated atoms. We see that molecules are much more strongly bound than the corresponding molecules with fermionic constituents. The binding energy increases rapidly with $Z$. In contrast, in the standard model molecular binding energy is of the order of few eVs in all cases (column 6). These facts suggest that molecules in a susy background would have much lower reaction cross sections than the diatomic molecules in our broken susy background.

From the second derivative of the energy at the minimum one can estimate the first vibrational energy level.

$$\frac{1}{2}\hbar\omega = \frac{\hbar}{2}\sqrt{\frac{d^2 <H>}{dR^2}/M} \tag{3.1}$$

where $M$ is the nuclear mass. From the curve of figure 1 we can estimate that the vibrational ground state lies, in the case of $O_2$, 4.4 eV or 0.3% above the minimum of the potential. This compares with 0.196 eV in the case of the usual $O_2$ molecule. [7].

In summary, the tendency of bosonic electrons to accumulate in the low-energy regions leads to strongly bound atoms and molecules in a susy world. In a susy atom all electrons occupy the $1s$ orbital in the ground state, leading to a spherical shape whose radius decreases as $1/Z_{eff}$, and the total energy scales as - $Z_{eff}^2$. The important point is that nuclear charge is only partially shielded, so that $Z_{eff} \propto Z$, which leads to ionization energies and electron affinities that increase rapidly with increasing $Z$. Similarly, atoms strongly bind to form molecules with binding energies that increase rapidly with $Z$. For example, a binding energy of 1471 eV for $O_2$ corresponds to a dissociation temperature of $\sim 10^7 K$. These properties have important consequences for bulk matter in the susy universe. It suggests that com-

plex molecules with larger number of atoms would form easily and that solids might have high melting points. Of course, macroscopic systems would exhibit Bose condensation and superfludity with high critical temperature.

The situation is very different in our universe, where only valence electrons take part in chemical reactions and molecular bonding, as they occupy the outermost orbitals due to the Pauli principle. The other electrons are effectively frozen out as they occupy the inner orbitals; their primary function is to shield the nuclear charge, which they do quite efficently. Consequenly $Z_{eff} \sim 1$, and ionization energies and electron affinities, and molecular binding energies are all of order a few eVs for all atoms.

As in every variational calculation, the accuracy can be improved and the energy estimate lowered by adding additional variational parameters. Asymptotically, the exact ground state energy will be approached from above. In the case of $H_2$ an improved energy was obtained [9] in the early days by adding a single parameter corresponding to a term in the wave function where both electrons were centered on the same nucleus. Reference [9] found a value of 4.0 eV for the dissociation energy compared to the experimental value of 4.7 eV.

For higher molecules similar refinements of the wave function would lead to an improvement in energy, but the main results are not expected to change qualitatively. In the case of a single atom, the key issue is the screening of the nuclear charge. Obviously the result can be improved by using the self-consistent Hartree-Fock approximation, in which the one-particle wave function $u(\vec{r})$ in 2.2 itself is determined variationally. Because of the spherical symmetry, the screening electric field seen by an electron at $\vec{R}$ is due to the fraction of the other $N-1$ electrons that are within the sphere of radius $R$. Hence the average screening charge is given by

$$Q_{scr}(R) = -(N-1)e \int_0^R dr 4\pi r^2 u^2(r) \quad . \tag{3.2}$$

Since the function $u(r)$ is the same for all electrons, a finite fraction of each electron is outside the sphere. Only when $R \to \infty$, does the integral equal unity, and $Q_{scr} = -(N-1)e$. On the other hand, suppose we take $R$ to be the most probable distance, obtained by minimizing $r^2 u^2(r)$. Then roughly half the particles will be outside the sphere of radius R, and hence roughly half of $Z$ nuclear charge will be unscreened. This means that, $Z_{eff} \propto Z$. Note that this argument does not depend on the precise form of $u(r)$. Hence, our results are qualitatively correct. Similar quantitative improvement can be achieved by introducing two-body (so called) Jastrow factors of the form $\prod_{ij} f(\vec{r}_i - \vec{r}_j)$ in the wave function, which take into account correlation effects by keeping particles away from each other. The problem then becomes intractable for large $Z$. However, we do not expect the qualitative physics to change.

For molecules results can also be improved by including admixtures of ionic configurations – that is, configurations with $Z+m$ particles centered on one atom, and $Z-m$ atoms centered on the other, with the relative amplitude determined variationally. These effects will lower the energy, and thus make the molecules even more strongly bound. However, since the transition to exact susy is unlikely to occur in the near cosmological future, it does not seem urgent at this time to seek an accuracy beyond that obtained by our present approximation.

# A    Overlap Integrals

Since the wave function is totally symmetric in the $2N$ electron positions, overlap integrals can be written as the number of permutations $(2N)!/N!^2$ times the overlap of a reference configuration with the full wave function. For the reference configuration we take the wave function where the first $N$ (scalar) electrons are in $1s$ states concentrated around the nucleus at position $\vec{R}$ while the remaining electrons are concentrated at $-\vec{R}$.

$$\Psi_{ref} = N_0(N) \left( \prod_{i=1}^{N} u(\vec{r}_i - \vec{R}) \right) \left( \prod_{j=N+1}^{2N} u(\vec{r}_j + \vec{R}) \right) = | - - \ldots - + + \ldots + > \quad \text{(A.1)}$$

Then the matrix element of any operator takes the form

$$< \Psi|\mathcal{O}|\Psi > = N_0(N)^2 \binom{2N}{N} < \Psi_{ref}|\mathcal{O}|\Psi_{ref} + perms > \quad . \quad \text{(A.2)}$$

If $\mathcal{O} = 1$ we have the normalization condition of eq. 2.16 with

$$A_0 = < -|+ > = \frac{Z_s^3}{\pi} \int d^3 r e^{-Z_s|\vec{r}-\vec{R}|-Z_s|\vec{r}+\vec{R}|} = e^{-2R'}(1 + 2R' + 4R'^2/3) \quad \text{(A.3)}$$

where

$$R' = Z_s R \quad \text{(A.4)}$$

The Hamiltonian consists of a sum over single particle terms and two particle terms. Its expectation value is given by a combinatoric sum over single and double particle expectation values. For instance

$$I_1 = < -|-\nabla^2|- > = < +|-\nabla^2|+ > = -\frac{1}{\pi} \int d^3 r e^{-2|\vec{r}|}(1 - 2/|\vec{r}|) = 1 \quad \text{(A.5)}$$

and

$$A_1 = < -|-\nabla^2|+ > = < +|-\nabla^2|- > = \int d^3 r u(\vec{r} - \vec{R})(-\nabla^2)u(\vec{r}+\vec{R})$$

$$= e^{-2R'}(1 + 2R' - 4R'^2/3) \quad \text{(A.6)}$$

The electron-nucleus interaction involves the integrals

$$I_2 = < -|\frac{1}{|\vec{r} - \vec{R}|}|- > \ = < +|\frac{1}{|\vec{r} + \vec{R}|}|+ > = 1 \quad \text{(A.7)}$$

$$A_{2a} = < -|\frac{1}{|\vec{r} + \vec{R}|}|- > = < +|\frac{1}{|\vec{r} - \vec{R}|}|+ > \quad \text{(A.8)}$$

$$A_{2b} = 2 < -|\frac{1}{|\vec{r} \pm \vec{R}|}|+ > = 2 < +|\frac{1}{|\vec{r} \pm \vec{R}|}|- > \quad \text{(A.9)}$$

It is easy to show that

$$A_{2a} = -1 + (1 + \frac{1}{2R'})(1 - e^{-4R'}) \tag{A.10}$$

$$A_{2b} = 2e^{-2R'}(1 + 2R') \tag{A.11}$$

The electron-electron repulsion term involves the two body integrals

$$I_3 = <--|\frac{1}{|\vec{r_1} - \vec{r_2}|}|-->=<++|\frac{1}{|\vec{r_1} - \vec{r_2}|}|++> \tag{A.12}$$

$$A_{3a} = <-+|\frac{1}{|\vec{r_1} - \vec{r_2}|}|-+>=<+-|\frac{1}{|\vec{r_1} - \vec{r_2}|}|+-> \tag{A.13}$$

$$A_{3b} = <-+|\frac{1}{|\vec{r_1} - \vec{r_2}|}|++>=<-+|\frac{1}{|\vec{r_1} - \vec{r_2}|}|--> \tag{A.14}$$

$$A_{3c} = <--|\frac{1}{|\vec{r_1} - \vec{r_2}|}|++>=<++|\frac{1}{|\vec{r_1} - \vec{r_2}|}|--> \tag{A.15}$$

All of the integrals of this appendix except for $A_{3b}$ occurred in the analysis of the $H_2$ molecule in the 1920's and were reviewed in the book of Pauling and Wilson [10]. We have added the evaluation of $A_{3b}$ since it occurs in the binding of the higher diatomic molecules in the susy case. The analytic expressions are

$$I_3 = 5/8 \tag{A.16}$$

$$A_{3a} = \frac{1}{2R'}(1 - e^{-4R'}) - e^{-4R'}(11/8 + 3R'/2 + 2R'^2/3) \tag{A.17}$$

$$A_{3b} = e^{-2R'}\left(\frac{1 - e^{-4R'}}{32R'}(5 + 4R') + 2R'\right) \tag{A.18}$$

and

$$\begin{aligned}
A_{3c} = \frac{1}{5}e^{-4R'}\Big( & 25/8 - 23R'/2 - 12R'^2 - 8R'^3/3 + \frac{6}{2R'}(1 + 2R' + 4R'^2/3)^2(\gamma + \ln(2R')) \\
& + \frac{6}{2R'}(e^{8R'}Ei(-8R')(1 - 2R' + 4R'^2/3)^2 \\
& - 2e^{4R'}Ei(-4R')(1 - 2R' + 4R'^2/3)(1 + 2R' + 4R'^2/3))\Big)
\end{aligned} \tag{A.19}$$

The exponential integral function Ei(x) goes asymptotically as $e^x$ which makes it convenient to factor out the overall $e^{-4R'}$ in eq. A.19. The complete expression for $A_{3c}$ was given in 1927 by Sugiura [11].

# B   Combinatorics

We consider a diatomic molecule with the two atoms centered at $\vec{R}$ and $-\vec{R}$, each with nuclear charge $Z$, with a total of $2N = 2Z$ electrons. However here, for greater generality, we take $Z$ and $N$ to be independent. The many-body wave function $\Psi$ is constructed from

single-paricle functions $u(\vec{r} \pm \vec{R})$ centered at $-\vec{R}$ and $\vec{R}$, respectively. The function $u(\vec{r})$ is similar, but not identical, to the atomic wave function, as it is calculated variationally.

The total wave function $\Psi$ is a linear combination of functions $\psi_m$ having $N+m$ particles centered at $-\vec{R}$ and $N - m$ particles centered at $\vec{R}$, with $-N \leq m \leq N$:

$$\psi_m = \prod_{i=1}^{N-m} u(\vec{r}_i - \vec{R}) \prod_{j=N-m+1}^{2N} u(\vec{r}_j + \vec{R}) + permutations \quad . \tag{B.1}$$

In calculating the expectation values we need to solve a combinatorial problem. This can be done in a compact way by introducing a pseudospin variable $\mu$ for each particle such that $\mu = 1$ or $-1$ if the particle is centered at $-\vec{R}$ and $\vec{R}$, respectively. Then $\sum_{i=1}^{2N} \mu_i = 2m$.

Let $u_\mu(\vec{r}) = u(\vec{r} + \mu\vec{R})$.

Then the ground-state wave function is given by

$$\Psi = \binom{2N}{N}^{-1/2} \sum_{m=-N}^{N} a_m \sum_{\{\mu\}} \delta_{m,\sum_j \mu_j/2} \prod_{i=1}^{2N} u_{\mu_i}(\vec{r}_i) \quad . \tag{B.2}$$

Where the $a_m$'s are variational parameters. By symmetry $a_m = a_{-m}$.

Consider first the evaluation of the normalization constant $< \Psi|\Psi >$ which has $2^{4N}$ terms, each of which is an integral over the $2N$ coordinates, and thus consists of $2N$ factors. We assume that each function $u_\mu(\vec{r})$ is normalized. But, in general, $u_\mu$ and $u_{-\mu}$ has a non-zero overlap $A_0$, so that

$$\int d^3 r u_\mu(\vec{r}) u_{\mu'}(\vec{r}) = \delta_{\mu,\mu'} + A_0 \delta_{\mu,-\mu'} \quad . \tag{B.3}$$

Then the normalization constant has the general form

$$< \Psi|\Psi >= \sum_{p=0}^{2N} Z_p A_0^p \tag{B.4}$$

where $Z_p$ is a combinatorial factor. To determine $Z_p$ consider orthonormal functions

$$v_n(q) = e^{2\pi i n q} \tag{B.5}$$

where $0 \leq q \leq 1$, and $n$ is an integer. Since

$$< v_m|v_n >= \int_o^1 dq e^{2\pi i (n-m)q} = \delta_{n,m} \quad , \tag{B.6}$$

we can represent the Kronecker $\delta$ in the wave function B.2 in a similar manner, leading to

$$\Psi = \binom{2N}{N}^{-1/2} \sum_{m=-N}^{N} a_m \sum_{\{\mu\}} \int_0^1 dq e^{-2\pi i m q} \prod_{j=1}^{2N} u_{\mu_j}(\vec{r}_j) e^{\pi i \mu_j q} \quad . \tag{B.7}$$

The representation allows us to integrate over $\vec{r}_i$ and sum over $\mu_i$ for each $i$ separately, which gives

$$< \Psi|\Psi > = \binom{2N}{N}^{-1} \sum_{m,m'} a_m a_{m'} \int_0^1 dq \int_0^1 dq' e^{2\pi i(m'q'-mq)}$$
$$\cdot \{e^{\pi i(q-q')} + e^{-\pi i(q-q')} + A_0(e^{\pi i(q-q')} + e^{-\pi i(q-q')})\}^{2N} \quad . \tag{B.8}$$

Expanding the factor $\{...\}^{2N}$, and integrating over $q, q'$ and after some rearrangements we finally obtain,

$$< \Psi|\Psi > = \sum_{m,m'} a_m a_{m'} \sum_{p=|m-m'|}^{2N-|m+m'|} F(N,p,m,m') A_0^p \quad . \tag{B.9}$$

where,

$$F(N,p,m,m') = \frac{N!N!\{1+(-1)^{(p+m+m')}\}}{2G} \tag{B.10}$$

with

$$G = \{N + (m+m'-p)/2\}!\{N - (m+m'+p)/2\}!\{(p+m-m')/2\}!\{(p+m'-m)/2\}! \quad .$$

Thus $F$ is zero unless $p + m + m'$ is even.

**Ground-State Energy:** To evaluate the energy $< \Psi|H|\Psi >$, let us write $H = H_1 + V_{ee}$, where $V_{ee}$ describes the electron-electron interaction, and

$H_1 = \sum_{i=1}^{2N} H_i$ is the sum of one-particle Hamiltonians $H_i$. We first consider $H_1$ whose average is given by $< \Psi|H_1|\Psi > = 2N < \Psi|H_i|\Psi >$ since the particles are identical. The evaluation of $< \Psi|H_i|\Psi >$ is similar to that of $< \Psi|\Psi >$ since the integration over the coordinates factorizes. Let

$$\int d^3 r_i u_\mu(\vec{r}_i) H_i u_{\mu'}(\vec{r}_i) = A_1 \delta_{\mu\mu'} + A_2 \delta_{\mu,-\mu'} \quad . \tag{B.11}$$

Proceeding as before, we obtain,

$$< \Psi|H_1|\Psi > = \sum_{m,m'} a_m a_{m'} I(m,m'), \tag{B.12}$$

where

$$I(m,m') = \sum_{p=|m-m'|}^{2N-|m+m'|} F(N,p,m,m')\{(2N-p)A_1 A_0^p + p A_2 A_0^{p-1}\} \quad . \tag{B.13}$$

Then the expectation value of the electron-electron term is given by

$$< \Psi|V_{e,e}|\Psi >= \frac{2N(2N-1)}{2} < \Psi|\frac{e^2}{|\vec{r_i} - \vec{r_j}|}|\Psi > \quad . \tag{B.14}$$

since all pairs yield the same expectation value. The procedure is similar, except that averaging over the pair interaction involves integrating over two coordinates. Let

$$B_1 = \int d^3r_1 d^3r_2 u_\mu^2(\vec{r_1}) \frac{e^2}{|\vec{r_i} - \vec{r_j}|} u_\mu^2(\vec{r_2}) \quad . \tag{B.15}$$

$$B_2 = \int d^3r_1 d^3r_2 u_\mu^2(\vec{r_1}) \frac{e^2}{|\vec{r_i} - \vec{r_j}|} u_{-\mu}^2(\vec{r_2}) \quad . \tag{B.16}$$

$$B_3 = \int d^3r_1 d^3r_2 u_\mu^2(\vec{r_1}) \frac{e^2}{|\vec{r_i} - \vec{r_j}|} u_\mu(\vec{r_2})u_{-\mu}(\vec{r_2}) \quad . \tag{B.17}$$

$$B_4 = \int d^3r_1 d^3r_2 u_\mu(\vec{r_1})u_{-\mu}(\vec{r_1}) \frac{e^2}{|\vec{r_i} - \vec{r_j}|} u_\mu(\vec{r_2})u_{-\mu}(\vec{r_2}) \quad . \tag{B.18}$$

Then we have

$$< \Psi|V_{e,e}|\Psi >= V_1 + V_2 + V_3 + V_4, \tag{B.19}$$

where

$$V_1 = \sum_{p=|m-m'|}^{2N-|m+m'|} F(N,p,m,m')\{(2N-p)(2N-p-2)+(m+m')^2\}B_1 A_0^p/4 \quad . \tag{B.20}$$

$$V_2 = \sum_{p=|m-m'|}^{2N-|m+m'|} F(N,p,m,m')\{(2N-p)^2-(m+m')^2\}B_2 A_0^p/4 \quad . \tag{B.21}$$

$$V_3 = \sum_{p=|m-m'|}^{2N-|m+m'|} F(N,p,m,m')(2N-p)pB_3 A_0^{p-1} \quad . \tag{B.22}$$

$$V_4 = \sum_{p=|m-m'|}^{2N-|m+m'|} F(N,p,m,m')\frac{B_4}{4}\{\left(p(p-2)+(m-m')^2\right)A_0^{p-2}$$
$$+ \left((2N-p)^2-(m+m')^2\right)A_0^p\} \quad . \tag{B.23}$$

**Heitler-London limit:** In this case we keep only $m = m' = 0$, so that each atom contains exactly $N$ electrons. As $R \to \infty$, the molecule dissociates into two isolated atoms in their respective ground states. We can set $a_0 = 1$.

Then we have

$$< \Psi|\Psi >= \sum_{k=0}^{N} \binom{N}{k}^2 A_0^{2k}. \tag{B.24}$$

$$< \Psi |H_1| \Psi >= \sum_{k=0}^{N} \binom{N}{k}^2 \{2(N-k)A_0^{2k}A_1 + 2kA_0^{2k-1}A_2\}. \tag{B.25}$$

$$< \Psi |V_{e,e}| \Psi >= \sum_{k=0}^{N} \binom{N}{k}^2 \left( A_0^{2k}\{(N-k)(N-k-1)B_1 + (N-k)^2(B_2+B_4)\} \right.$$
$$\left. + 4k(N-k)A_0^{2k-1}B_3 + k(k-1)B_4 A_0^{2k-2} \right). \tag{B.26}$$

If we include $m, m' = \pm 1$, there is one extra variational parameter $a_1 = a_{-1}$. These contribute the following terms to $< \Psi | \Psi >$:

$$\sum_{k=0}^{N} \binom{N}{k}^2 A_0^{2k}\{4a_1 A_0 \frac{N-k}{k+1} + 2a_1^2(\frac{N-k}{N-k+1} + \frac{k}{k+1})\}. \tag{B.27}$$

This analysis is given for completeness and as a guide to future improvements only. In the current paper, numerical results are presented for the $m = m' = 0$ term only.

# References

[1] Jason Kumar, Int. J. Mod. Phys. *A21*, 3441 (2006)

[2] Steven Giddings, hep-th/0303031, *Phys. Rev.* **D68**,026006 (2003).

[3] Katherine Freese and Douglas Spolyar, hep-th/0412145, JCAP 0507:007 (2005)

[4] W. Heitler and F. London, *Z.f.Phys.***44**,455 (1927)

[5] L. Clavelli and T. Lovorn, *IJMP***A22**, 2133 (2007)

[6] F. Hund, *Z.f.Phys.* **51**, 73 (1928)

[7] K.P. Huber and G. Herzberg, *Constants of Diatomic Molecules* Van Nostrand Reinhold, New York (1979).

[8] S.C. Wang,*Phys. Rev.***31**,579 (1928)

[9] S. Weinbaum, *J. Chem. Phys.***1**, 593 (1933)

[10] L. Pauling and E.B. Wilson, *Introduction to Quantum Mechanics*, McGraw-Hill, New York (1935).

[11] Y. Sugiura, *Z.f.Phys.***45**, 484 (1927)