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I hereby recommend that the thesis prepared under my supervision by Carl A. Ludeke
entitled

Part I  A Vibration Method of Testing Materials
Part II  Interchange Energy

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

[Signatures]

Harold J. Kester  Part I
Boris Podolsky  Part II
J. A. Wells  Chairman
Part I

A VIBRATION METHOD OF TESTING MATERIALS

A dissertation submitted to the

Graduate School
of the University of Cincinnati

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

1938

by

Carl Arthur Ludeke

A.B. University of Cincinnati 1935
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I. Introduction

Among the well known tests applied to materials, are those for tensile strength, elongation, fatigue stresses, and hardness.

Tensile strength can be measured under constant load or under impact. For a test under constant load, a standard piece is gripped between the upper and lower jaws of a machine and the total resistance to rupture is measured. The tensile strength is usually given in pounds per square inch. For a measurement under impact, the material is ruptured by the blow of a heavy pendulum. The tensile strength is given by a number which corresponds to the height attained by the pendulum after breaking the test piece. See Fig. 1.

![Tensile Strength Diagram](image)

**TENSILE STRENGTH**

**CONSTANT LOAD**

**IMPACT**

**LBS. / SQ. IN.**

Figure 1.
Elongation is measured in percent of the original test section and is commonly the amount of stretch which will occur in the material when pulled apart by tension. It is usually measured in relation to an initial distance of two inches. In Fig. 2., as the material stretches, the two metal arms fastened to the test piece move apart and allow the wedge to move to the left. The motion of this wedge is communicated to a pen which traces, on a revolving drum, a curve which shows the elongation as a function of the force used in breaking the specimen.

**ELONGATION**

![Elongation Diagram]

**RESULTS IN PERCENT**

*Figure 2.*

Fatigue tests are made by applying forces of varying magnitude and direction to a test piece and noting the number of times the piece withstands this strain before
breaking. Figure 3. shows two types of fatigue tests.

FATIGUE

REVOLUTIONS TO BREAK

Figure 3.
In the diagram on the left, a thin test rod is supported at each end and weighted in the middle. The rod, curved under this weight, is rotated until it breaks. On the right, a thin test strip is clamped at one end and then vibrated to and fro. In both cases the result is given in revolutions necessary to break the test specimen.

Hardness is usually measured by impressing a diamond or steel point into the material to be tested and noting the dimensions of the indentation made. Figure 4. gives three types of hardness tests.
Figure 4.

In the Vicker's test a diamond point is used and a square indentation made. The diagonal of the square is measured by a microscope. The magnitude of the diagonal is used as a measure of hardness. The Brinell test is very similar, using however a steel ball instead of a diamond point. In this case the diameter of the indentation is used as a measure of hardness. In the Rockwell test no microscope is used. A guage measures the depth of the indentation made by a steel ball. The reading of the guage is used as a measure of hardness.

These are only a few of the tests commonly made to determine the suitability of a material for various
purposes and to insure uniform quality of the material. However, we notice two characteristics common to each of these tests. They are:

(1) The result in each case is represented by a single number.

(2) Each test involves numerous properties of the material which can not be disentangled. That is, in each of these tests we do not understand exactly what we are measuring but we do know that these measurements can be used as a check on the quality of the material.

Having briefly reviewed some of the more common tests applied to materials I must now explain what led me to a new method of testing. For a long time it has been a well known fact among bell makers that all metals are not equally suitable for bells and that certain heat treatments greatly increased the duration of sound emitted by bells. Thus we are faced with two problems. First, we must in some way assign to each material a number which will serve as an index of its vibration properties. Second, we must find how this number varies with heat treatment.

At first an attempt was made to measure with a stop watch the duration of sound emitted by a material when caused to vibrate. This leads to at least one serious difficulty. The human ear must determine exactly when
the sound ceases to be audible; and since the sound diminishes gradually, this is very difficult to do. Thus to investigate the problem we must in some way determine the decrement curve of the vibrating material. That is, we must know the rate of change of amplitude with time while the amplitude is still sufficiently large to make measurements upon it. Therefore let us attempt to answer the question, "What is decrement curve of a vibrating bar rigidly clamped at one end?".

If we assume that the energy dissipated by vibration is used solely in disturbing the surrounding medium we have no means of explaining the change in the decrement curve due to heating; because externally at least, the material remains the same. Therefore, let us consider the decrement curve in relation to the internal structure of the bar.

In any vibrating system the amplitude slowly diminishes unless energy is supplied to the system. In the case of a bar clamped at one end, part of the energy is absorbed by the support, part is dissipated by the internal friction of the bar, and part is used in disturbing the surrounding medium. In order to calculate the energy dissipated by internal friction, let us postulate that the bar is made of rows of crystals which slide upon each other as the bar vibrates.
II. Theoretical

Let $E$ be the energy of the vibrating system.

$-\frac{dE}{dt}$ is the rate of decrease of the energy.

If the forces causing this decrease in $E$ are frictional, we can say:

$-\frac{dE}{dt}$ is proportional to the force between sliding surfaces.

$-\frac{dE}{dt}$ is proportional to the sliding distance.

We assume that the amplitude is always small compared to the length of the bar and that the form of the bar always approximates the arc of a circle.

Let us now determine the force between surfaces.

The force on an element of surface $ds$ long and $dw$ wide is proportional to the curvature, which is the reciprocal of the radius of curvature. For a circle, curvature equals $1/r$ where $r$ is the radius of the circle. Therefore the force between layers in a bar of length unity and width $w$ is given by

$$F \propto \frac{1}{r} f(w)$$

where $F$ is the force per unit length, and $f(w)$ is some function of the width.

In order to determine $f(w)$ we must examine how the pressure in the horizontal direction varies with the width. From X-ray photographs we know that the crystals
in the bar are not arranged with their sides parallel to the sides of the bar. Hence we have a component of pressure in the horizontal direction. Consider the cross section of a bar with pressure applied perpendicularly to its width.

Due to the horizontal pressure the bar bulges at the edges, and in doing so increases the pressure between the sides of the crystals near the edge of the bar. But we developed the theory for vertical pressure as if we had a thin section out of the middle of an infinite sheet. Thus we see that the horizontal pressure is less in the middle of the bar than it is near the edges. Therefore the "effective width" of the bar is much greater than its actual width. Since the edge effect would be constant with various widths and of greater relative importance with smaller widths, we say:

\[ f(w) = w + k \]

where \( w \) is the actual width, and \( k \) is a constant to compensate for edge effect. (\( k \) may be larger than \( w \)) Thus we have:

\[ F = l/r (w + k) \]
We must now determine the sliding distance. Consider a bar made of only two layers of crystals. The average distance \( D \) that the layers will slide on each other when the bar moves from its present position to zero amplitude is given by

\[
D \propto \frac{\phi}{2\pi} \left( 2\pi(r+d) - 2\pi r \right)
\]

\( D \propto \phi d \)

For a bar of many layers

\( D \propto \phi c \)

where \( c \) is the thickness of the bar.

Therefore the sliding distance per unit length of the bar is proportional to \( \frac{\phi c}{2} \).

But

\( F \propto \frac{l}{r} (w+k) \)

Thus the energy dissipated by a unit length of the bar is proportional to

\[ \frac{\phi c}{2} \frac{(w+k)}{r} \]

Therefore the energy dissipated by the bar is proportional to

\[ \frac{\phi c}{r} (w+k) = \frac{1}{2} \frac{c}{r} (w+k) \quad \text{since} \quad \phi = \frac{l}{r} . \]
The equation of the form of the bar is:

\[(y - r)^2 + x^2 = r^2\]

\[y^2 - 2yr + x^2 = 0\]

If \(A << l\), then \(s \approx l = \text{constant}\)

Therefore the coordinates of the end of the bar are \((l,A)\)

\[A^2 - 2Ar + l^2 = 0\]

\[\frac{A^2 + l^2}{2A} = r; \quad \frac{1}{r} = \frac{2A}{A^2 + l^2} = \frac{2A}{l^2} \left(\frac{1}{A^2/l^2 + 1}\right) \approx \frac{2A}{l^2}\]

Thus \(1/r \propto A/l^2\)

Therefore the energy dissipated by the bar is proportional to

\[\frac{A^2}{l^3} c(w+k)\]

The energy dissipated per cycle is proportional to

\[\frac{c(w+k)}{l^3} \int_0^{A_{\text{max}}} A^2 dA \propto \frac{c(w+k)}{l^3} A_{\text{max}}^3\]

Since the frequency is approximately constant we have

\[-\frac{dE}{dt} \propto \frac{c(w+k)}{l^3} A_m^3\]

But \(E \propto A_m^2\) from which \(A \frac{dA}{dt} \propto \frac{dE}{dt}\) (I have dropped the \(m\).)
Therefore

$$\frac{-\partial A}{\partial t} \propto \frac{\omega (w+k)}{L^3} A^2$$

Integrating this we find:

$$\frac{1}{A} = \frac{\omega (w+k)}{L^3} t + \frac{1}{A_0}$$

This would be the decrement curve if no energy were lost to the support and to the medium. Because of this additional loss of energy, for each value of $t$, $A$ will be less than this equation predicts. Therefore let us assume that the corrected equation can be written:

$$\frac{1}{A + \delta} = \frac{\omega (w+k)}{L^3} t + \frac{1}{A_0 + \delta}$$

Where

- $\omega$ is a constant of the material
- $c$ is the thickness
- $w+k$ is the effective width
- $w$ is the actual width
- $L$ is the length
- $\delta$ is a constant introduced to compensate for the energy lost to the support and to the medium.
III. Experimental

In order to test this equation the following apparatus was constructed. See Fig. 5.

Figure 5.

The bar is rigidly clamped in a vise which is firmly fastened to the wall. On the free end of the bar is a small aluminum holder, on the face of which is a tiny mirror at a 45 degree angle to the length of the bar. The mirror is illuminated by a 50 candle power auto bulb. The rear of the camera consists of a slide along which an electric motor drives, at a uniform rate of speed, a 5" x 7" Graflex film holder.
The bar is set in motion by a striking mechanism which works as follows: (See Fig. 6.)

**STRIKING MECHANISM**

![Diagram of striking mechanism]

**Figure 6.**
As the hammer falls upon the bar it strikes the trigger and releases the sliding catch. This allows the spring to expand and keep the hammer from striking the bar more than once.

Difficulty was encountered in getting a suitable spot of light. In order to get a curve with fairly sharp edges, it is necessary that the spot be very small. See top diagram of Figure 7.
Figure 7.

Because of the finite image of the spot which is formed on the film, for large amplitudes the curve consists of a heavy inner line and a faint outer line. The heavy inner line is caused by the overlapping of the spot images. For small amplitudes the two lines coincide and give the curve a sharp edge.

At first a small mirror was cemented on the aluminum holder and all but a small circle of mirror's surface was painted black. (Lower left hand diagram of Fig. 7.) However, because of the smooth surface of the mirror, the portion painted black reflected too much light.
Next, black paper was tried, but it was difficult to cut a small opening in the paper without leaving a fuzzy edge. Finally, four strips of photographic tape were pasted on the mirror so as to obscure all of its surface except a 1 mm. square. This worked satisfactorily.

A test was made to determine if results were reproduceable. This would constitute a check on the uniform motion of the film holder, and on the effect of clamping in the vise. The test was made on two bars of cold rolled steel 20.00 cm long, 1.27 cm. wide, and 0.15 cm. thick. For each bar three pictures were taken, the bar being removed and then reinserted in the vise for each picture. The results were:

Bar #1

<table>
<thead>
<tr>
<th>t</th>
<th>A</th>
<th>A</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.53</td>
<td>3.53</td>
<td>3.53</td>
</tr>
<tr>
<td>2</td>
<td>1.42</td>
<td>1.39</td>
<td>1.40</td>
</tr>
<tr>
<td>4</td>
<td>0.78</td>
<td>0.74</td>
<td>0.75</td>
</tr>
<tr>
<td>6</td>
<td>0.45</td>
<td>0.44</td>
<td>0.45</td>
</tr>
<tr>
<td>8</td>
<td>0.30</td>
<td>0.28</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Bar #2

<table>
<thead>
<tr>
<th>t</th>
<th>A</th>
<th>A</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.53</td>
<td>3.53</td>
<td>3.53</td>
</tr>
<tr>
<td>2</td>
<td>1.44</td>
<td>1.42</td>
<td>1.45</td>
</tr>
</tbody>
</table>
This does not show that the vise absorbs none of the energy, but it does show that the effect of the vise is the same in each case and the motion of the film holder is the same in each case.

Since nothing was said in the theoretical development of the equation as to how the bar is to be set in motion, the following test was made. The bar was caused to vibrate first by striking and then by pulling it downward with a thread and burning the thread. The resulting decrement curves were:

Bars of cold rolled steel 20.00 cm. long, 1.27 cm. wide, and 0.15 cm. thick.

<table>
<thead>
<tr>
<th>t</th>
<th>A (Struck)</th>
<th>A (Held with thread)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.53</td>
<td>3.53</td>
</tr>
<tr>
<td>2</td>
<td>1.42</td>
<td>1.39</td>
</tr>
<tr>
<td>4</td>
<td>.72</td>
<td>.72</td>
</tr>
<tr>
<td>6</td>
<td>.44</td>
<td>.42</td>
</tr>
<tr>
<td>8</td>
<td>.28</td>
<td>.28</td>
</tr>
</tbody>
</table>
Bar #2

<table>
<thead>
<tr>
<th>t</th>
<th>A (Struck)</th>
<th>A (Held with thread)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.53</td>
<td>3.53</td>
</tr>
<tr>
<td>2</td>
<td>2.39</td>
<td>1.39</td>
</tr>
<tr>
<td>4</td>
<td>.72</td>
<td>.73</td>
</tr>
<tr>
<td>6</td>
<td>.42</td>
<td>.43</td>
</tr>
<tr>
<td>8</td>
<td>.28</td>
<td>.27</td>
</tr>
</tbody>
</table>

Thus, whether the bars were struck or held with thread, the resulting decrement curves were the same.

Finally, though the bars emitted no sound while vibrating, there was of course a metallic ping as the hammer struck the bar. By covering the hammer with felt the sound was reduced to a dull thud. Tests were made to see if this altered the decrement curve. The results were:

<table>
<thead>
<tr>
<th>t</th>
<th>A (Lead hammer)</th>
<th>A (Felt hammer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.55</td>
<td>3.55</td>
</tr>
<tr>
<td>2</td>
<td>2.05</td>
<td>2.07</td>
</tr>
<tr>
<td>4</td>
<td>1.29</td>
<td>1.30</td>
</tr>
<tr>
<td>6</td>
<td>.88</td>
<td>.88</td>
</tr>
<tr>
<td>8</td>
<td>.65</td>
<td>.65</td>
</tr>
</tbody>
</table>
Brass

<table>
<thead>
<tr>
<th>t</th>
<th>A (Lead hammer)</th>
<th>A (Felt hammer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.53</td>
<td>3.53</td>
</tr>
<tr>
<td>2</td>
<td>1.97</td>
<td>1.96</td>
</tr>
<tr>
<td>4</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>6</td>
<td>.70</td>
<td>.71</td>
</tr>
<tr>
<td>8</td>
<td>.46</td>
<td>.46</td>
</tr>
</tbody>
</table>

Having satisfactorily tested the apparatus, it was now time to test the equation. For a particular size of bar the equation can be written

\[
\frac{1}{A + \delta} = \beta t + \frac{1}{A_0 + \delta}
\]

where \( \beta \) is a constant. This is in the form of a straight line if we plot \( \frac{1}{A + \delta} \) against \( t \); \( \beta \) being the slope and \( \frac{1}{A_0 + \delta} \) the y intercept.

Doing this for a copper bar 23.00 cm. long, 0.56 cm. wide, and 0.15 cm. thick, we get the following results. Our \( t \) is measured in units of 1.3 seconds, the time required for the film holder to move 1 cm.
<table>
<thead>
<tr>
<th>t</th>
<th>A (Experimental)</th>
<th>A (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.43</td>
<td>3.43</td>
</tr>
<tr>
<td>1</td>
<td>2.78</td>
<td>2.73</td>
</tr>
<tr>
<td>2</td>
<td>2.26</td>
<td>2.24</td>
</tr>
<tr>
<td>3</td>
<td>1.86</td>
<td>1.87</td>
</tr>
<tr>
<td>4</td>
<td>1.59</td>
<td>1.58</td>
</tr>
<tr>
<td>5</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>6</td>
<td>1.15</td>
<td>1.16</td>
</tr>
<tr>
<td>7</td>
<td>1.00</td>
<td>1.01</td>
</tr>
<tr>
<td>8</td>
<td>.87</td>
<td>.88</td>
</tr>
<tr>
<td>9</td>
<td>.76</td>
<td>.77</td>
</tr>
<tr>
<td>10</td>
<td>.68</td>
<td>.68</td>
</tr>
</tbody>
</table>

Equation

$\frac{1}{A + .67} = .050t + .244$

$\delta$ was determined by trial and error.

Thus we see that our theoretical equation satisfies experimental results.

If we plot a graph of experimental values we have:

![Graph of experimental values](image)
In order to test the equation, bars of different widths and lengths were cut from a sheet of copper 0.15 cm. thick. Consider a set of 5 bars 0.15 cm. thick and 23.00 cm. long, but of various widths. The experimental results were:

<table>
<thead>
<tr>
<th>Width</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56 cm.</td>
<td>0.050</td>
</tr>
<tr>
<td>0.72</td>
<td>0.054</td>
</tr>
<tr>
<td>0.93</td>
<td>0.061</td>
</tr>
<tr>
<td>1.08</td>
<td>0.063</td>
</tr>
<tr>
<td>1.25</td>
<td>0.065</td>
</tr>
</tbody>
</table>

where

\[
\beta = \frac{\xi c (w + k)}{\ell^2}
\]

Before we can evaluate \( \xi \) we must find \( k \). Since in each case the thickness, length, and material of the bar is the same, the following equation is true.

\[
\frac{\beta_2}{\beta_1} = \frac{w_1 + k}{w_2 + k}
\]

or

\[
\frac{\beta_2^{w_1} - \beta_1^{w_2}}{\beta_1 - \beta_2} = k
\]
By inserting the above values of \( w \) and \( \beta \) into this equation and taking the average of the results, we find that \( k = 1.5 \). The value of \( \xi \) can now be calculated, and if the form of \( f(w) \) is correct, we should find that \( \xi \) is a constant. The results were:

<table>
<thead>
<tr>
<th>( w )</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.56</td>
<td>( 1.97 \times 10^3 )</td>
</tr>
<tr>
<td>0.72</td>
<td>1.97</td>
</tr>
<tr>
<td>0.93</td>
<td>2.03</td>
</tr>
<tr>
<td>1.08</td>
<td>1.98</td>
</tr>
<tr>
<td>1.25</td>
<td>1.92</td>
</tr>
</tbody>
</table>
We now consider a set of 5 bars 0.15 cm. thick, 0.56 cm. wide, but of different lengths. The experimental results:

<table>
<thead>
<tr>
<th>Length (cm.)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.40</td>
<td>0.136</td>
</tr>
<tr>
<td>17.90</td>
<td>0.104</td>
</tr>
<tr>
<td>19.40</td>
<td>0.081</td>
</tr>
<tr>
<td>20.90</td>
<td>0.067</td>
</tr>
<tr>
<td>23.00</td>
<td>0.050</td>
</tr>
</tbody>
</table>

Since we are using the same material as before, \( k \) will remain 1.50, and hence we can solve for \( \sigma \). If \( \beta \) contains \( l \) in the proper relation, \( \sigma \) will be constant and should be the same as the previous \( \sigma \). We find:

<table>
<thead>
<tr>
<th>Length (cm.)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.40</td>
<td>1.93 x 10^3</td>
</tr>
<tr>
<td>17.90</td>
<td>1.94</td>
</tr>
<tr>
<td>19.40</td>
<td>1.92</td>
</tr>
<tr>
<td>20.90</td>
<td>1.98</td>
</tr>
<tr>
<td>23.00</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Thus we see that the form of our equation is correct and that it contains the dimensions in the proper relation.
IV. Examples of the Vibration Method of Testing

At this point we see that we have answered the first question which suggested this research. That is, we have assigned to every material a number which serves as an index of its vibration properties. This number we call $\gamma$, the vibration modulus. (If we test bars of the same size we can use $\beta$ in stead of $\gamma$.) The results of tests made on several materials are:

<table>
<thead>
<tr>
<th>Material</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>.115</td>
</tr>
<tr>
<td>Iron</td>
<td>.110</td>
</tr>
<tr>
<td>Yellow Brass</td>
<td>.075</td>
</tr>
<tr>
<td>Spring Brass</td>
<td>.069</td>
</tr>
<tr>
<td>Phosphor Bronze</td>
<td>.065</td>
</tr>
</tbody>
</table>

\[
\frac{1}{A + .67} = \beta t + \frac{1}{A_0 + .67}
\]

Thus as we descend the list of materials the internal friction becomes less.

We turn now to an investigation of the manner in which $\beta$ varies with heat treatment. We shall limit
ourselves to temperatures of 500 degrees Centigrade. Various bars were heated for one hour and allowed to cool in air. The qualitative results are given in Figure 10.

![Graph showing the increase in the value of \( \beta \) for iron, the decrease for copper, and no change for brass.](image)

**Figure 10.**

From these results we see that such heat treatments increase the value of \( \beta \) for iron, lower it for copper, bronze, and chime metal, and leave unchanged the value of \( \beta \) for brass. Before making a quantitative test for copper, bronze, and brass, a test was made to see if the value of \( \beta \) could be further diminished by heat treating.
the bars for more than one hour. The results were:

![Graph showing the relationship between time and a variable β.]

**Figure 11.**

We see that the curve reaches a minimum at about 45 minutes. Thus I continued to use one hour as the time of heat treatment. The results on copper, brass, and bronze are given in Figure 12.
Figure 12.

Thus I have answered the two questions which gave birth to this thesis, and in doing so I believe I have introduced a new method of testing.
Appendix

Usually no attempt is made to derive the decrement equation from considerations of internal friction. Instead, the decrement curve is taken to be exponential in form and is written:

\[ A = A_0 e^{-kt} \]

where \( A \) is the amplitude at time \( t \)

\[ A_0 \] " " " " " " \( t = 0 \)

\( k \) is the number which represents the ability of a bar to continue in vibration.

Using this equation, which fits the experimental results approximately, the results recorded on Figure 12 take on the form shown in Figure 13.

Figure 13.
Part II

INTERCHANGE ENERGY

A dissertation submitted to the

Graduate School
of the University of Cincinnati

in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY

1938

by

Carl Arthur Ludeke

A.B. University of Cincinnati 1935
V. Fock, in the *Zeitschrift fur Physik*, Volume 61, 1930, page 126, gives as the equation of energy for a system of electrons:

\[ W = \int \sum_{i=1}^{n+1} \psi_i^*(x)H(x)\psi_i(x)dx + \frac{e^2}{2} \int \frac{\rho(x)\rho(x'x') - |\rho(x'x')|^2}{|r - r'|} dx dx' \]

where \( W \) is the energy of the system.

\( n+1 \) is the number of electrons of the system.

\( H(x) \) is the energy operator of a single electron.

\( \psi_i(x) \) (\( i=1, 2, \cdots, n+1 \)) are the wave functions of each electron in the system.

\[ \rho(x'x') = \sum_{i=1}^{n+1} \overline{\psi_i(x)}\psi_i(x') \]

For the case of two free electrons the potential energy is given by:

\[ E = \frac{e^2}{2} \int \frac{\rho(x)\rho(x'x') - |\rho(x'x')|^2}{|r - r'|} dx dx' \]

where \( E \) is the energy of the two electrons and

\[ \rho(x'x') = \overline{\psi_1(x)}\psi_1(x') + \overline{\psi_2(x)}\psi_2(x') \]

In the expression for \( E \),

\[ \frac{e^2}{2} \int \frac{\rho(x)\rho(x'x')}{|r - r'|} dx dx' \]

represents the Coulomb energy

\[ -\frac{e^2}{2} \int \frac{|\rho(x'x')|^2}{|r - r'|} dx dx' \]

represents the interchange energy.
It is the purpose of this paper to evaluate the expressions for Coulomb energy and interchange energy. With this in mind, wave packets for the electrons are introduced. On page 271 in Volume 117 of the Proceedings of the Royal Society, C. G. Darwin gives as the wave packet for an electron at time $t = 0$,

$$\exp \left[ -\frac{1}{\mathcal{Q}} \left\{ \frac{(x-x_0)^2}{\mathcal{Q}^2} + \frac{(y-y_0)^2}{\mathcal{Z}^2} + \frac{(z-z_0)^2}{\mathcal{V}^2} \right\} \right]
+ \frac{i2\pi\hbar}{h} \{u(x-x_0) + v(y-y_0) + w(z-z_0)\}$$

where $\mathcal{Q}$ is the uncertainty in $x$

$\mathcal{Z}$ " " " y

$\mathcal{V}$ " " " z

$u$ is the velocity in the $x$ direction

$v$ " " " " " y

$w$ " " " " " z

$(x_0, y_0, z_0)$ is the initial position of the electron.

In the problem to be treated, the velocity of both electrons is taken to be the same.
Thus for a spherical distribution,

\[ \psi_2(x) = N \exp \left[ -\frac{1}{2} \left\{ \frac{(x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2}{\sigma^2} \right\} \right] \\
+ \frac{12\pi m}{\hbar} \left\{ u(x-x_0) + v(y-y_0) + w(z-z_0) \right\} \]

and if particle \( l \) is at the origin,

\[ \psi_1(x) = N \exp \left[ -\frac{1}{2} \left\{ \frac{x^2 + y^2 + z^2}{\sigma^2} \right\} + \frac{12\pi m}{\hbar} \left\{ ux + vy + wz \right\} \]

where \( N \) is a normalizing factor. That is,

\[ N^2 \int \psi_2(x) \psi_2(x) \, dv = 1. \quad \text{It is found that} \quad N = \frac{1}{n^{3/4} \sigma^{3/2}} \]

Before beginning any evaluations, consider the integral

\[ \int_{-\infty}^{\infty} e^{-p^2(a^2 + b^2 + c^2)} \, da \, db \, dc. \]

This can be written

\[ 2\pi \int_{0}^{\pi} \int_{0}^{\pi} e^{-p^2 r^2} r^2 dr \, d\theta \, d\varphi = 4\pi \int_{0}^{\infty} e^{-p^2 r^2} r^2 dr \]

In Dwight, Tables of Integrals, page 176, formula 861.7 gives

\[ \int_{0}^{\infty} x^{2a} e^{-px^2} \, dx = \frac{1 \cdot 3 \cdot 5 \cdot \ldots \cdot (2a-1)}{(\pi/p)^{1/2}} \frac{1}{2a+1} \quad p^a \]

From which

\[ \int_{0}^{\infty} e^{-p^2 r^2} r^2 \, dr = \frac{\pi^{3/2}}{4p^3} \]

*The need and value of \( N \) was suggested to me by Dr. Podolsky.*
Consider the Coulomb energy given by the equation

\[ \frac{e^2}{2} \int \frac{\rho(x)\rho(x')}{|r - r'|} \, dx \, dx' \]

where \( \rho(x) = \overline{\psi}_1(x)\psi_1(x) + \overline{\psi}_2(x)\psi_2(x) \)

\( \rho(x'x') = \overline{\psi}_1(x')\psi_1(x') + \overline{\psi}_2(x')\psi_2(x') \)

\( \rho(x)\rho(x'x') = N^4 \left\{ \overline{\psi}_1(x)\psi_1(x)\overline{\psi}_1(x')\psi_1(x') \right. \\
\left. + \overline{\psi}_2(x)\psi_2(x)\overline{\psi}_2(x')\psi_2(x') + \overline{\psi}_1(x)\psi_1(x)\overline{\psi}_2(x')\psi_2(x') \right. \\
\left. + \overline{\psi}_2(x)\psi_2(x)\overline{\psi}_2(x')\psi_2(x') \right\} \)

\( \overline{\psi}_1(x)\overline{\psi}_1(x)\overline{\psi}_1(x')\psi_1(x') = \)

\[ \exp \left[ -\frac{1}{\sigma^2} (x^2 + y^2 + z^2) \right] \exp \left[ -\frac{1}{r'^2} (x'^2 + y'^2 + z'^2) \right] \]

Therefore

\[ \int\int\int e^{-\frac{1}{\sigma^2}(x^{2}+y^{2}+z^{2})} \, dx' \, dy' \, dz' \int\int\int e^{-\frac{1}{r'^{2}}(x'^{2}+y'^{2}+z'^{2})} \, dx \, dy \, dz \]

\[ \left[ (x-x')^2 + (y-y')^2 + (z-z')^2 \right]^{\frac{1}{2}} \]

must be evaluated. Let \( x-x' = X \), \( y-y' = Y \), and \( z-z' = Z \).

Hence, the integral becomes:

\[ \int\int\int e^{-\frac{1}{\sigma^2}(x^{2}+y^{2}+z^{2})} \, dx' \, dy' \, dz' \int\int\int e^{-\frac{1}{r'^{2}}\left\{X^2 + Y^2 + Z^2 + (X+Y+Z)^2\right\}} \, dx \, dy \, dz \]

\[ \left[ X^2 + Y^2 + Z^2 \right]^{\frac{1}{2}} \]

which can be written:
\[ \iiint e^{-\frac{1}{4\sigma^2}(x^2 + y^2 + z^2)} \, dx \, dy \, dz \leq \iiint e^{-\frac{2}{\pi} (x' + y' + z')^2} \, dx' \, dy' \, dz' \]

\[ = \frac{\pi^{3/2}}{2^{3/2}} \int e^{-\frac{1}{4\sigma^2}(a^2 + b^2 + c^2)} \, da \, db \, dc = \frac{\pi^{3/2}}{2^{3/2}} \]

because \[ \iiint e^{-\frac{1}{4\sigma^2}(a^2 + b^2 + c^2)} \, da \, db \, dc = \frac{\pi^{3/2}}{2^{3/2}} \]

Therefore integral (1) can now be written:

\[ \frac{\pi^{3/2}}{2^{3/2}} \iiint \exp \left[ \frac{1}{4\sigma^2} (x^2 + y^2 + z^2) \right] dx \, dy \, dz \]

\[ = \frac{\pi^{3/2}}{2^{3/2}} \int e^{-\frac{1}{\sigma^2} R^2} R^2 \, dR = \frac{2^{1/2} \pi^{5/2}}{2^{3/2}} \sigma^5 \]

Thus integral (1) equals \( 2^{1/2} \pi^{5/2} \sigma^5 \).

Consider next the integral due to the term

\[ \bar{\psi}_2(x) \bar{v}_2(x) \bar{\psi}_2(x') \bar{v}_2(x') = \]

\[ \exp \left[ -\frac{1}{4\sigma^2} \left( (x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 \right) \right] \exp \left[ \frac{1}{\sigma^2} (x'_0 - x_0)^2 + (y'_0 - y_0)^2 + (z'_0 - z_0)^2 \right] \]
Let $X = x-x_0$ and $X' = x'-x_0$ etc.

Thus the integral to be evaluated is:

$$\iiint \exp \left[ -\frac{i}{\hbar} \left( x'^2 + y'^2 + z'^2 \right) \right] dx' dy' dz' \iiint \exp \left[ \frac{i}{\hbar} \left( x^2 + y^2 + z^2 \right) \right] dx dy dz$$

$$\left[ (x-x')^2 + (y-y')^2 + (z-z')^2 \right]^{1/2}$$

(2)

This is the same as integral (1) and is equal to $2^{3/2} \frac{\pi^{5/2}}{\sqrt{5}}$

Consider the term $\Psi_2(x)\Psi_2(x)\Psi_1(x')\Psi_1(x') = \exp \left[ \frac{i}{\hbar} \left( (x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 \right) \right] \exp \left[ \frac{i}{\hbar} \left( x'^2 + y'^2 + z'^2 \right) \right]$

which yields the integral

$$\iiint \exp \left[ \frac{i}{\hbar} \left( (x-x_0)^2 + (y-y_0)^2 + (z-z_0)^2 \right) \right]$$

$$\left[ (x-x')^2 + (y-y')^2 + (z-z')^2 \right]^{1/2}$$

(3)

$$\left[ (x+y+y_0)^2 + (z+z_0)^2 \right]^{1/2}$$

where $X' = x'-x$, $Y' = y'-y$, and $Z' = z'-z$.

This can be written

$$\iiint \exp \left[ \frac{i}{\hbar} \left( \frac{(x'^2 + y'^2 + z'^2)}{2} + \frac{(x^2 + y^2 + z^2)}{2} \right) \right]$$

$$\left[ (x-x')^2 + (y-y')^2 + (z-z')^2 \right]^{1/2}$$

$$\times \exp \left[ \frac{i}{\hbar} \left( \frac{(x+y+y_0)^2 + (z+z_0)^2}{2} \right) \right] dx dy dz dx' dy' dz'$$

which becomes

$$\iiint \exp \left[ \frac{i}{\hbar} \left( (x+x_0)^2 + (y+y_0)^2 + (z+z_0)^2 \right) \right]$$

$$\left[ (x'^2 + y'^2 + z'^2) \right]^{1/2}$$

$$\frac{r^{3/2} \sqrt{5}}{2^{3/2}}$$

$$\frac{\pi^{5/2}}{\sqrt{5}}$$
This integral in polar coordinates is:

\[
\frac{\pi^{3/2} \sigma^{3}}{2^{3/2}} \int_{0}^{2\pi} \int_{0}^{\pi} \frac{d\phi}{\sin \theta} \int_{0}^{\infty} \exp\left[-\frac{1}{2\sigma^{2}} (R^{2} + r_{o}^{2})\right] R' \, dR'
\]

If \( r_{o} \) is in the \( z \) direction this equation becomes:

\[
\frac{\pi^{5/2} \sigma^{3}}{2^{3/2}} \int_{0}^{\infty} \exp\left[- \frac{r_{o}^{2}}{2\sigma^{2}} \right] R' \, dR' \int_{0}^{\pi} \exp\left[-\frac{r_{o} R' \cos \theta}{\sigma^{2}}\right] \sin \theta \, d\theta
\]

\[
= \pi^{5/2} \frac{5}{2} \sigma^{3} \int_{0}^{\infty} \exp\left[-\frac{r_{o}^{2}}{2\sigma^{2}} \right] \int_{0}^{\pi} \exp\left(-\frac{r_{o} R' \cos \theta}{\sigma^{2}}\right) \sin \theta \, d\theta
\]

In order to integrate this, consider the integral

\[
\int_{P_{1}}^{P_{2}} \exp(p \sigma) \, dp = \exp\left(-\frac{\sigma^{2}}{4a}\right) \int_{p_{1}}^{P_{2}} \exp\left[-\frac{1}{2}a^{2} \left(\frac{p}{\sigma^{2}}\right)^{2} \right] \, dp
\]

\[
= \frac{1}{\sqrt{2\pi a^{2}}} \int_{\frac{p_{1}}{\sigma}}^{\frac{P_{2}}{\sigma}} \exp\left(-x^{2}\right) \, dx
\]

Therefore

\[
\int_{0}^{\infty} \exp(p \sigma + a \sigma^{2}) \, dp = \frac{1}{\sqrt{2\pi a^{2}}} \exp\left(-\frac{\sigma^{2}}{4a}\right) \left[1 - \text{erf}\left(\frac{\sigma}{2a^{2/3}}\right)\right]
\]
With the use of this integral,
\[
\int \left[ \exp \left( -\frac{1}{2} \frac{R'^2}{\sigma^2} + \frac{r_o R'}{\sigma^2} \right) - \exp \left( -\frac{1}{2} \frac{R'^2}{\sigma^2} - \frac{r_o R'}{\sigma^2} \right) \right] dR' = 2^{\frac{3}{2}} \pi^{\frac{3}{2}} \exp \left( \frac{r_o^2}{2 \sigma^2} \right) \text{erf} \left( \frac{r_o}{\sqrt{2} \sigma} \right)
\]

Thus integral (3) is equal to \( \frac{n^6}{r_o} \text{erf} \left( \frac{r_o}{\sqrt{2} \sigma} \right) \)

\[
\int \frac{\overline{\psi}_1(x) \psi_1(x) \overline{\psi}_2(x') \psi_2(x')}{|r - r'|} \, dx dx' \quad (4)
\]

is equal to \( \int \frac{\overline{\psi}_2(x) \psi_2(x) \overline{\psi}_1(x') \psi_1(x')}{|r - r'|} \, dx dx' \)

which is integral (3). Therefore integral (4) equals \( \frac{n^6}{r_o} \text{erf} \left( \frac{r_o}{\sqrt{2} \sigma} \right) \).

Coulomb energy = \( N^4 \frac{e^2}{2} \left\{ f(1) + f(2) + f(3) + f(4) \right\} \)

\[
= \frac{e^2}{\pi^{\frac{3}{2}}} \sigma^{\frac{1}{2}} + \frac{e^2}{r_o} \text{erf} \left( \frac{r_o}{\sqrt{2} \sigma} \right)
\]
Consider now the integration of the interchange term,

\[ \iint \frac{|\rho(x'x)|^2}{|r-r'|} \, dx \, dx' \quad \text{where} \quad \rho(x'x) = \overline{\psi_1(x)} \psi_1(x') + \overline{\psi_2(x)} \psi_2(x') \]

Let \( \overline{\psi_1(x)} \psi_1(x') = e^{p+iq} \), and \( \overline{\psi_2(x)} \psi_2(x') = e^{r+is} \).

\[ \rho(x'x) = e^{p+iq} + e^{r+is} \]

\[ |\rho(x'x)|^2 = e^{2p} + e^{2r} + e^{(p+r)+(q-s)i} + e^{(p+r)-(q-s)i} \]

From page 2,

\[ iq = -\frac{i2m}{h}(ux + vy + wz) + \frac{i2m}{h} (ux' + vy' + wz') \]

\[ is = -\frac{i2m}{h} \left\{ u(x-x_o) + v(y-y_o) + w(z-z_o) \right\} \]

\[ + \frac{i2m}{h} \left\{ u(x'-x_o) + v(y'-y_o) + w(z'-z_o) \right\} \]

\[ \therefore iq - is = 0 \quad \text{and} \quad |\rho(x'x)|^2 = e^{2p} + e^{2r} + 2e^{(p+r)} \]

\[ p = -\frac{1}{2\eta^2} (x^2 + x'^2 + y^2 + y'^2 + z^2 + z'^2) \]

\[ e^{2p} = e^{-\frac{1}{\eta^2}(x^2+y^2+z^2)} e^{-\frac{1}{\eta^2}(x'^2+y'^2+z'^2)} \]

Thus the term \( e^{2p} \) yields integral (1) on page 4, and is therefore equal to \( 2^\frac{3}{2} \pi^{5/2} q^{-5} \).
\[ r = \frac{1}{4\pi} \left[ (x-x_o)^2 + (y-y_o)^2 + (z-z_o)^2 + (x'-x_o)^2 + (y'-y_o)^2 + (z'-z_o)^2 \right] \]

Thus \( e^{2r} \) yields integral (2), on page 6, which is equal to \( 2^{\frac{3}{2}} \pi \frac{5}{2} \sqrt{5} \).

\[ p+r = \frac{1}{4} \left\{ \left( \frac{x-x_o}{2} \right)^2 + \left( \frac{y-y_o}{2} \right)^2 + \left( \frac{z-z_o}{2} \right)^2 + \left( \frac{x'-x_o}{2} \right)^2 + \left( \frac{y'-y_o}{2} \right)^2 \right\} \]

\[ + \left( \frac{z'-z_o}{2} \right)^2 + \frac{x_o^2 + y_o^2 + z_o^2}{2} \]

Let \( x-x' = X \), \( y-y' = Y \), and \( z-z' = Z \).

\[ p+r = \frac{1}{4} \left\{ \left( \frac{X}{2} \right)^2 + \left( \frac{Y}{2} \right)^2 + \left( \frac{Z}{2} \right)^2 \right\} \]

\[ + \frac{x_o^2 + y_o^2 + z_o^2}{2} + \frac{x'^2 + y'^2 + z'^2}{2} \]

\[ 2\int e^{p+r} \frac{dxdydz}{|r-r'|} = \]

\[ 2\int \frac{\exp\left[ -\frac{1}{2} \left( x_o^2 + y_o^2 + z_o^2 + (x^2 + y^2 + z^2) \right) \right]}{\left[ x^2 + y^2 + z^2 \right]^\frac{1}{2}} \]

\[ x\int \exp\left[ -\frac{1}{2} \left( \frac{x+x_o}{2} \right)^2 + \left( \frac{y+y_o}{2} \right)^2 + \left( \frac{z+z_o}{2} \right)^2 \right] \]

\[ \frac{dxdydz}{\left[ x^2 + y^2 + z^2 \right]^\frac{1}{2}} \]

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\[= 2 \exp\left(-\frac{r_o^2}{2} \varphi^2\right) \int_0^{2\pi} \int_0^\pi \sin \theta \, d\theta \exp\left(-\frac{R^2}{2} \varphi^2\right) R dR \frac{\pi^{3/2} \varphi^{-3}}{3/2} \]

\[= 2^{3/2} \pi^{5/2} \varphi^{-5} \exp\left(-\frac{r_o^2}{2} \varphi^2\right) \]

- Interchange energy

\[= N \frac{4 \pi e^2}{2} \left\{ 2\left(2^{\frac{3}{2}} \pi^{5/2} \varphi^{-5}\right) + 2^{3/2} \pi^{5/2} \exp\left(-\frac{r_o^2}{2} \varphi^2\right) \right\} \]

\[= \frac{e^2}{\varphi \pi \varphi} + \frac{e^2}{\varphi \pi \varphi} \exp\left(-\frac{r_o^2}{2} \varphi^2\right) \]
Consider now an interpretation of the results,

Coulomb energy = \( \frac{e^2 \frac{1}{2} \frac{3}{2}}{\sqrt{\pi} \frac{3}{2}} + \frac{e^2}{r_o} \operatorname{erf}(r_o/2 \frac{3}{2} \varpi) \)

- Interchange energy = \( \frac{e^2 \frac{3}{2}}{\sqrt{\pi} \frac{3}{2}} + \frac{e^2 \frac{3}{2}}{\sqrt{\pi} \frac{3}{2}} \exp(-r_o^2/2 \varpi^2) \)

\[ E = \frac{e^2}{r_o} \operatorname{erf}(r_o/2 \frac{3}{2} \varpi) - \frac{e^2 \frac{3}{2}}{\sqrt{\pi} \frac{3}{2}} \exp(-r_o^2/2 \varpi^2) \]

where \( e \) is the charge on the electron.

\( r_o \) is the distance between electrons.

\( \varpi \) is the spherical uncertainty of position.

\( E \) is the total energy of the two electrons.

As a check on the final result for \( E \), use is made of the fact that, when \( r_o = 0 \) the system is reduced to one electron and \( E \) is zero.

\[ \frac{e^2}{r_o} \operatorname{erf}(r_o/2 \frac{3}{2} \varpi) = \frac{e^2}{r_o} \frac{2}{\sqrt{\pi} \frac{3}{2}} \left( \frac{r_o}{2 \frac{3}{2} \varpi} - \frac{r_o^3}{3 \varpi^{3/2}} + \frac{r_o^5}{5 \varpi^{5/2}} \right) \text{ etc.} \]

which equals \( \frac{e^2 \frac{3}{2}}{\sqrt{\pi} \frac{3}{2}} \) when \( r_o = 0 \) and \( \varpi \neq 0 \).

\[ \frac{-e^2 \frac{3}{2}}{\sqrt{\pi} \frac{3}{2}} \exp(-r_o^2/2 \varpi^2) = \frac{-e^2 \frac{3}{2}}{\sqrt{\pi} \frac{3}{2}} \text{ when } r_o = 0 \text{ and } \varpi \neq 0. \]

Therefore \( E = 0 \) when \( r_o = 0 \) and \( \varpi \neq 0 \).
In the expressions for Coulomb energy and interchange energy, \( \frac{e^2}{r_o} \) is the self energy of the two electrons; and, as is proper, this term disappears in the expression for the total energy. Thus the Coulomb energy is given by

\[
\frac{e^2}{r_o} \text{erf}(r_o/2^\frac{3}{2} \sqrt{\pi})
\]

which is correct; because as \( \sqrt{\pi} \) approaches 0, this expression approaches \( \frac{e^2}{r_o} \).

The interchange term,

\[
\frac{e^2}{\sqrt{\pi} r_o^3} \exp(-r_o^2/2 \sqrt{\pi}^2) \rightarrow 0 \text{ as } \sqrt{\pi} \rightarrow 0,
\]

because

\[
\lim_{\sqrt{\pi} \rightarrow 0} \frac{e^2}{\sqrt{\pi} r_o^3} \exp(-r_o^2/2 \sqrt{\pi}^2) = \lim_{x \rightarrow \infty} \frac{2e^2}{\pi^\frac{3}{2}} x \exp(-r_o^2 x^2)
\]

\[
= \lim_{x \rightarrow \infty} \frac{2e^2}{\pi^\frac{3}{2}} x \frac{x}{\exp(r_o^2 x^2)} = 0.
\]

Thus, when the position of both particles is known exactly,

\[
E = \frac{e^2}{r_o}.
\]
In order to make a numerical table of the relative importance of Coulomb energy and interchange energy, the expression for $E$ is written in the following form:

$$E = \frac{e^2}{r_0} \text{erf}(0.707 \frac{r_0}{\sigma}) - 0.798 \frac{r_0}{\sigma} \exp(-r_0^2/2 \sigma^2)$$

$$= \frac{e^2}{r_0} (C-I) \quad \text{where} \quad \frac{C e^2}{r_0} = \text{Coulomb energy}$$

$$I \frac{e^2}{r_0} = \text{Interchange energy}$$

Following, is a table of $C$, $I$, and $C-I$, for various values of $r_0/\sigma$.

<table>
<thead>
<tr>
<th>$r_0/\sigma$</th>
<th>$C$</th>
<th>$I$</th>
<th>$C-I$</th>
<th>$r_0/\sigma$</th>
<th>$C$</th>
<th>$I$</th>
<th>$C-I$</th>
</tr>
</thead>
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<td>0.080</td>
<td>0.080</td>
<td>0.000</td>
<td>1.1</td>
<td>0.729</td>
<td>0.479</td>
<td>0.250</td>
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<td>0.157</td>
<td>0.001</td>
<td>1.2</td>
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<td>0.362</td>
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<td>0.017</td>
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</tr>
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