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Submitted on 1 Jan 1969

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EXCHANGE POLARIZATION OF THE 3d-SHELL AND ISOTOPE SHIFT OF THE LEVELS Cu II 3d⁹ 4s ¹D AND ³D

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Abstract. — According to the first-order theory of the specific-mass effect the ¹D- and ³D-levels of 3d⁹ 4s-configuration in the Cu II-(and Ni I-) spectrum are expected to have the same isotopic displacement. Measurements indicate, however, that there is a difference which amounts to 4 mK in the case of copper (δM = 2) and 4 mK in the case of nickel (δM = 6). An attempt is made to ascribe this behaviour to a difference in the 3d-orbitals of ¹D and ³D states, respectively. Within a configurational interaction model this may be described by admixtures of 3d⁹ 4s 4d states to 3d⁹ 4s 4d states. The amplitudes of these admixtures differ in the cases of ¹D and ³D states. They are proportional to the Slater parameter R₉(3d 4s, 4s 4d) and inversely proportional to the distance of the configurations 3d⁹ 4s and 3d⁹ 4d 4s in the zero-order approximation. These admixtures alter the specific-mass effect of the 3d-shell with the filled 2p- and 3p-shells by amounts which are proportional to J(3d, 2p)·J(4d, 2p) and J(3d, 3p)·J(4d, 3p) where the symbols J denote the well-known integrals of Vinti. These integrals are calculated numerically by means of Hartree-Fock functions which have been given partly by Hartree, partly they result from our own calculation. The agreement of the measured and the calculated values is satisfactory and apt to give a new impression of the origin of isotopic shifts in this region of the periodic system.

1. Introduction. — The first-order theory of mass-depandant isotope-shift which has been worked out by Hughes and Eckart [1], Bartlett and Gibbons [2] and Vinti [3] can explain some features of the measured shifts in the spectra of light elements. But there are examples where it fails, as well. For instance this theory predicts that all the levels of an electronic configuration should have the same shift provided the following condition holds: The configuration should not contain electrons with orbital quantum numbers differing by exactly one unit. Closed shells are excluded from this condition. In accordance with this rule the levels 4s 4p ¹P and 4s 4p ³P in Zn I-spectrum possess unequal isotope shifts. Consequently this phenomenon had been referred to the existence of a Hughes-Eckart-integral J(4p, 4s) by Crawford and others [4].

Measurements, however, in the Cu II-spectrum [5] and in the Ni I-spectrum [6] indicate that the levels 3d⁹ 4s ¹D and 3d⁹ 4s ³D possess unequal shifts, as well. This phenomenon contradicts the quoted rule. The results are in detail:

\[ \langle 3d^9 4s ¹D | \delta(\sigma) | 3d^9 4s ¹D \rangle - \langle 3d^9 4s ³D | \delta(\sigma) | 3d^9 4s ³D \rangle = 4 \text{ mK} \]
for the nuclide Ni$^{64}$ as compared to the nuclide Ni$^{58}$
\[
< 3d^9 4s \, ^1D \mid \delta(\sigma) \mid 3d^9 4s \, ^1D > =
\]
= < 3d$^9$ 4s $^3D \mid \delta(\sigma) \mid 3d^9 4s \, ^3D > = 4.7 \text{ mK}
for the nuclide Cu$^{65}$ as compared to the nuclide Cu$^{63}$.

(Positive isotope shift means that the hypothetical transition $3d^9 \, 4s \, ^1D \rightarrow 3d^9 \, 4s \, ^3D$ is shifted towards higher frequencies for the heavier nuclide as compared to the lighter one.)

There are other topics which disagree with Hughes' and Eckart's theory. Look at figure 1. There the residual shift of Cu$^{II}$-3d$^9$ nl levels is plotted against the mean distance of the nl electron from the nucleus.

Residual shift means isotope shift less normal shift. Therefore it equals the specific mass effect plus volume effect. The residual shift increases from 4s to 4p. Then it remains constant to even higher excited electrons thus representing the residual shift of the ionization limit. But the Hughes-Eckart-theory would predict that the residual shift should decrease instead of increasing when the 4s electron is removed because then it would no longer contribute to the total specific mass effect with the terms $2 \frac{m_e}{M} \frac{M}{M_1} \frac{M}{M_2} \text{ Ry} \sum \frac{J^2 (np \, 4s)}{\pi}$.

Recent calculations of Bauche [7] concerning specific mass effect in Cu I-spectrum (1) show that the rise of the specific mass effect accompanying the excitation of the 4s-electron is due to changes of the 3d-eigenfunctions. The radial functions of the 3d-electrons are affected by the removal of the 4d-electron in such a way that the Hughes-Eckart integrals $J(3 \, d, \, 2 \, p)$ and $J(3 \, d, \, 3 \, p)$ are increased markedly thus accounting for the increase of the total specific mass effect. Bauche's calculations have been repeated by the authors with Cu I-eigenfunctions of Synk [8]. The results are given in table 1 exhibiting clearly the behaviour just described. The agreement with Bauche's results is fairly good.

Let us now consider how the 4s electron influences the 3d electrons. The strongest influence arises from the direct screening of the 3d electron by the 4s charge cloud. But the exchange interaction between 3d and 4s electrons should not be overlooked completely because it is the latter kind of interaction which may influence the 3d electrons of the $^1D$ and the $^3D$ in a different way. This we need in order to explain the different isotope shift of $^1D$ and $^3D$.

FIG. 1.—Residual shifts of some configurations of the Cu II spectrum.

FIG. 2.—Calculated radial functions of some s electrons in the copper ion.

(1) The specific mass effect in the Cu I-spectrum increases in the same manner as it does in the Cu II spectrum when the 4s electron is exited or even removed.
Calculated specific mass effects of some Cu I states. Synek's functions were used. $J^2$ denotes $J^2(nl, n'l - 1)$, $nl, n'l - 1$ being specified at the top of the table.

**Table 1**

<table>
<thead>
<tr>
<th>Level</th>
<th>$m\Delta M$</th>
<th>$(2p, 1s)$</th>
<th>$(2p, 2s)$</th>
<th>$(2p, 3s)$</th>
<th>$(2p, 4s)$</th>
<th>$(3p, 1s)$</th>
<th>$(3p, 2s)$</th>
<th>$(3p, 3s)$</th>
<th>$(3p, 4s)$</th>
<th>$(4p, 1s)$</th>
<th>$(4p, 2s)$</th>
<th>$(4p, 3s)$</th>
<th>$(3d, 2p)$</th>
<th>$(3d, 3p)$</th>
<th>$(3d, 4p)$</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 d$^{10}$4 s$^{1}$g$^{2}$</td>
<td>$\delta \sigma = 29.438$ mK</td>
<td>$</td>
<td>4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 2\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 2\ 1^{2}\ +\ 8\ 1^{2}\ +\ 8\ 1^{2}</td>
<td>$</td>
<td>$16\ 235$ mK+124.9 mK+233.5 mK+3.1 mK+1 699 mK+946.8 mK+142.6 mK+10.0 mK</td>
<td>$+3\ 396$ mK+841.4 mK</td>
<td>$-23\ 633$ mK</td>
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<tr>
<td>3 d$^{10}$4 p$^{1}$p$^{2}$</td>
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</tr>
<tr>
<td>3 d$^{10}$3 s$^{1}$</td>
<td>$\delta \sigma = 29.438$ mK</td>
<td>$</td>
<td>4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 2\ 1^{2}\ +\ 2\ 1^{2}\ +\ 8\ 1^{2}\ +\ 8\ 1^{2}\ +\ 4\ 1^{2}</td>
<td>$</td>
<td>$16\ 235$ mK+124.9 mK+233.5 mK+3.1 mK+1 697 mK+945.8 mK+142.3 mK</td>
<td>$2.4$ mK+1.3 mK+0.3 mK+3 413 mK+841.4 mK+0.8 mK</td>
<td>$-23\ 641$ mK</td>
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<tr>
<td>3 d$^{10}$4 s$^{1}$p$^{1}$</td>
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<tr>
<td>3 d$^{10}$4 d$^{1}$</td>
<td>$\delta \sigma = 29.438$ mK</td>
<td>$</td>
<td>4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 8\ 1^{2}\ +\ 8\ 1^{2}</td>
<td>$</td>
<td>$16\ 235$ mK+124.9 mK+233.5 mK+3.1 mK+1 697 mK+945.4 mK+142.4 mK</td>
<td>$+3\ 419$ mK+845.4 mK</td>
<td>$-23\ 642$ mK</td>
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<tr>
<td>3 d$^{10}$4 f$^{1}$</td>
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</tr>
<tr>
<td>3 d$^{10}$4 s$^{1}$f$^{1}$</td>
<td>$\delta \sigma = 29.438$ mK</td>
<td>$</td>
<td>4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}\ +\ 4\ 1^{2}</td>
<td>$</td>
<td>$16\ 235$ mK+125.0 mK+236.3 mK+8.8 mK+1 723 mK+960.7 mK+142.4 mK+27.5 mK</td>
<td>$+3\ 333$ mK+758.9 mK</td>
<td>$-23\ 549$ mK</td>
<td></td>
<td></td>
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</tbody>
</table>
The configuration $3d^8\, nd\, 4s$ gives rise to a variety of $^1D$ and $^3D$ states which all may share in the perturbation of $3d^9\, 4s\, ^1D$ and $^3D$. These are

1. for $3d^9\, 4s\, ^1D$

\[
(3d^8)^1S(nd\, 4s)^1D^1D \\
(3d^8)^3P(nd\, 4s)^3D^1D \\
(3d^8)^1D(nd\, 4s)^1D^1D \\
(3d^8)^3F(nd\, 4s)^3D^1D \\
(3d^8)^1G(nd\, 4s)^1D^1D
\] (1)

2. for $3d^9\, 4s\, ^3D$

\[
(3d^8)^1S(nd\, 4s)^3D^3D \\
(3d^8)^3P(nd\, 4s)^3D^3D \\
(3d^8)^1D(nd\, 4s)^3D^3D \\
(3d^8)^3F(nd\, 4s)^3D^3D \\
(3d^8)^1G(nd\, 4s)^3D^3D
\]

Generally we shall write

\[
(3d^8)^1S(nd\, 4s)^3D^3D
\]

These states occur with amplitudes in the perturbed states $^1D, ^3D$ (2) which can be given to the first order by the equation

\[
< [(3d^8)^1S(nd\, 4s)^3D^3D] \, (3d^8)^1S(nd\, 4s)^3D^3D > = (3d^8(SL\, 3d^2D) \, 3d^8(S^2D) \, \sqrt{2(2S' + 1)} \, W(S' \frac{1}{2} 0 \frac{1}{2} 0) \times \]

\[
\times \sqrt{9} \frac{R^0(3d\, 4s, nd\, 4s) + (-1)^S \, R^2(3d\, 4s, 4s\, nd)/S}{\epsilon_{3d} - \epsilon_{nd}} \] (3)

\[
< [(3d^8)^1S(nd\, 4s)^3D^3D] \, (3d^8)^3D^3D > = (3d^8(SL\, 3d^2D) \, 3d^8(S^2D) \, \sqrt{2(2S' + 1)} \, W(S' \frac{1}{2} 0 \frac{1}{2} 0) \times \]

\[
\times \sqrt{9} \frac{R^0(3d\, 4s, nd\, 4s) + (-1)^S \, R^2(3d\, 4s, 4s\, nd)/S}{\epsilon_{3d} - \epsilon_{nd}} \] (4)

The amplitudes eq. (3) and (4) were calculated by evaluating the matrix elements of the electrostatic interaction of $3d^9\, 4s\, ^1D, ^3D$ with anyone of the excited states of (1) and (2). In order to take advantage of the selection rules of this interaction one decouples the interacting $3d$-electron of $3d^9\, 4s\, ^1D, ^3D$ coupling it afterwards to the $4s$-electron. Thus one expands the states $(3d^9\, 4s)^1D, ^3D$ to the states

\[
(3d^8)^SL(3d\, 4s)^1D, ^3D.
\]

The first coefficient denotes a well-known «coefficient of fractional parentage» occurring when one $3d$ electron is decoupled from the $3d^9$ shell. The second coefficient which is a Racah-coefficient results from the recoupling of the spin of the $3d$ electron. The coefficient $\sqrt{9}$ results from the fact that each of the nine $3d$ electrons of $3d^9\, 4s$ may interact with the $nd$-electron of $3d^9\, nd\, 4s$. This point is more thoroughly discussed in a paper of Rosenzweig [9]. The $R^0$ and $R^2$ are Slater-parameters the first of which accounts for the $3d$-$nd$ excitation by direct screening from the $4s$ electron. The second one accounts for the $3d$-$nd$ excitation by exchange polarization of the $3d$ shell by the $4s$ electron. Concerning the energy denominator it had been assumed that

(2) In the following the perturbed states which have been classified after $3d^9\, 4s\, ^1D, ^3D$ will be denoted by $^1D, ^3D$ without any specification of configuration.
the energetical difference of all the levels of $3d^8nd4s$ with respect to the levels of $3d^84s$ roughly equals the excitation energy of a single $3d$ electron to the $nd$ level. The coefficients of the expansion of

$$(3d^94s)^1D, 3D$$

to $[(3d^9) SL(3d4s) S' L']^1D, 3D$

have been given in table II.

### Table II

Coefficients which occur when the states $$(3d^94s)^1D, 3D$$
are expanded to the states $$[(3d^9) SL(3d4s) S' L']^1D, 3D$$

<table>
<thead>
<tr>
<th>S' S L (3d^9(SL)3d^2D) 3d^92D</th>
<th>\sqrt{2(2S' + 1)} W(S\frac{l}{2}0\frac{1}{2} S')</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 0</td>
<td>\sqrt{1/45}</td>
</tr>
<tr>
<td>1 1 1</td>
<td>\sqrt{9/45}</td>
</tr>
<tr>
<td>0 0 2</td>
<td>\sqrt{5/45}</td>
</tr>
<tr>
<td>1 1 3</td>
<td>\sqrt{21/45}</td>
</tr>
<tr>
<td>0 0 4</td>
<td>\sqrt{9/45}</td>
</tr>
</tbody>
</table>

The coefficients which arise from the expansion

$$(3d^8) SL(nd4s) S' L'$$

have been already given in table 2. The quantities $J$ are defined as

$$J(nl, n'l - 1) = a_0 \int_0^\infty R(n, l) \times$$

$$\times \left[ \frac{d}{dr} - \frac{l - 1}{r} \right] R(n', l - 1) r^2 dr.$$  

4. Numerical results and comparison with experiment. — All the quantities in question have been calculated using Hartree's functions. They are given in table III. The quantum number $n$ runs from 4 to 6. Details of the calculation of the excited nd-functions are communicated in chapter 5.

The values of table III are to be inserted into the final formulae (8) and (9) compiled from formulae (3), (4) and (6). They provide the specific mass effects of $(3d^94s)^1D$ and $(3d^94s)^3D$ as compared to the ionization limit $(3d^9)^2D$.

3. Non diagonal matrix elements of the specific mass effect with respect to the configurations $3d^94s$ and $3d^9nd4s$. — Non diagonal matrix elements of the specific mass effect exist between $3d^94s$ and $3d^94s$ and $3d^9nd4s$. They arise if the operator of the specific mass effect

$$\delta(\sigma) = \frac{1}{M} \sum_{i>j=1}^N p_i p_j$$

$$N = \text{total number of electrons in the atom}$$

puts into correlation an inner $p\{i\}$ electron of $3d^94s$ with the $nd\{i\}$-electron of $3d^9nd4s$ on the one hand and an inner $p\{j\}$ electron of $3d^9nd4s$ with any $3d\{j\}$ electron of $3d^94s$ on the other hand. The superscripts $\{i\}$ and $\{j\}$ denote the number of the electron's coordinates. All other electronic states should have the same electronic coordinates in both configurations for otherwise the matrix element of $\delta(\sigma)$ vanishes. The detailed calculation of the matrix element is greatly facilitated by the fact that the inner $p$-electron belongs to a closed shell. For this reason the matrix elements

$$< [(3d^9) SL(3d4s) S' L'] S'' L'' | \delta(\sigma) | [(3d^9) SL(nd4s) S' L'] S'' L'' >$$

are all degenerate with respect to $SL, S' L', S'' L''$ and equal the same value

$$\sqrt{9}(4/5) Ry(m_e \delta M/M_1M_2) \sum_m J(3d, mp) J(nd, mp).$$

From this one concludes

$$< [(3d^9) SL(nd4s) S' L']^1D, 3D | \delta(\sigma) | (3d^94s)^1D, 3D > =$$

$$= \left\{ \begin{array}{ll}
(3d^9(SL)3d^2D)3d^92D \sqrt{2(2S' + 1)} W(S\frac{l}{2}0\frac{1}{2} S') \times
\end{array} \right\}

\times \sqrt{9}(4/5) Ry(m_e \delta M/M_1M_2) (J(3d, 2p) J(nd, 2p) + J(3d, 3p) J(nd, 3p))$$

for $1D$

$$= \left\{ \begin{array}{ll}
(3d^8(SL)3d^2D)3d^92D \sqrt{2(2S' + 1)} W(S\frac{l}{2}1\frac{1}{2} S') \times
\end{array} \right\}

\times \sqrt{9}(4/5) Ry(m_e \delta M/M_1M_2) (J(3d, 2p) J(nd, 2p) + J(3d, 3p) J(nd, 3p))$$

for $3D$.
\[
<^{1}D | \delta(\sigma) |^{1}D > = - < (3d)^{2}D | \delta(\sigma) | (3d)^{2}D > = \\
= \frac{m_e \delta M}{M_1 M_2} Ry \left[ 2 J^2(2p, 4s) + 2 J^2(3p, 4s) + 2 \sum_{n=4} R^0(3d 4s, nd 4s) - \frac{1}{15} R^2(3d 4s, 4snd) \frac{1}{e_{3d} - e_{nd}} \times \right. \\
\left. \times \frac{36}{5} \left( J(3d, 2p) J(nd, 2p) + J(3d, 3p) J(nd, 3p) \right) \right] 
\]

\[
<^{3}D | \delta(\sigma) |^{3}D > = - < (3d)^{2}D | \delta(\sigma) | (3d)^{2}D > = \\
= \frac{m_e \delta M}{M_1 M_2} Ry \left[ 2 J^2(2p, 4s) + 2 J^2(3p, 4s) + 2 \sum_{n=4} R^0(3d 4s, nd 4s) - \frac{1}{9} R^2(3d 4s, 4snd) \frac{1}{e_{3d} - e_{nd}} \times \right. \\
\left. \times \frac{36}{5} \left( J(3d, 2p) J(nd, 2p) + J(3d, 3p) J(nd, 3p) \right) \right]. 
\]

**Table III**

<table>
<thead>
<tr>
<th>nd</th>
<th>( \varepsilon_{nd} ) Ry</th>
<th>( R^0(3d 4s, nd 4s) ) cm(^{-1} )</th>
<th>( R^2(3d 4s, 4snd) ) cm(^{-1} )</th>
<th>( J(nd, 2p) )</th>
<th>( J(nd, 3p) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td>- 1.621</td>
<td>-</td>
<td>-</td>
<td>- 8.912</td>
<td>- 3.80</td>
</tr>
<tr>
<td>4d</td>
<td>- 0.425</td>
<td>2.882</td>
<td>- 6.209</td>
<td>- 3.611</td>
<td>- 0.73</td>
</tr>
<tr>
<td>5d</td>
<td>- 0.250</td>
<td>1.427</td>
<td>- 3.611</td>
<td>- 0.44</td>
<td>- 0.07</td>
</tr>
<tr>
<td>6d</td>
<td>- 0.159</td>
<td>916</td>
<td>- 2.473</td>
<td>- 0.31</td>
<td>- 0.05</td>
</tr>
</tbody>
</table>

**Table IV**

Contributions of the particular terms of formulae (8) and (9) to the total specific mass effect of the \( 3d^{9} 4s^{1}D \) and \( ^{3}D \) terms in Cu II-spectrum.

| Kind of the contribution | \( <^{3}D | \delta(\sigma) |^{3}D > = - < \delta(\sigma) >_{\text{ion,lim.}} \) | \( <^{1}D | \delta(\sigma) |^{1}D > = - < \delta(\sigma) >_{\text{ion,lim.}} \) |
|-------------------------|--------------------------|--------------------------|
| 4 s-electron :          | 16.7 mK                  | 16.7 mK                  |
| excitation \( 3d \rightarrow 4d \) : | - 36.1 mK              | - 33.3 mK              |
| \( 3d \rightarrow 5d \) : | - 9.1 mK                 | - 8.3 mK                 |
| \( 3d \rightarrow 6d \) : | - 4.0 mK                 | - 3.6 mK                 |
| total :                 | - 32.4 mK                | - 28.5 mK                |

The numerical contributions of the particular terms of formulae (8) and (9) are listed in table IV. The results of table IV demonstrate the rise of the specific mass effect caused by the removal of the 4 s-electron from Cu II: \( 3d^{9} 4s \)-configuration. Excitation effects of the \( 3d \)-shell overcompensate the direct contribution of the 4 s-electron as expected in chapter 1. Moreover, the \( 3d^{9} 1D \)- and \( ^{3}D \)-states have different specific mass effect and the calculated value

\[
<^{1}D | \delta(\sigma) |^{1}D > = - <^{3}D | \delta(\sigma) |^{3}D > = 3.9 \text{ mK} 
\]

agrees well with the measured value 4.7 mK. The agreement is even improved if the higher orbitals

(3) Further computed values to be used in formulae (8) and (9) are \( J(2p, 4s) = 0.25 \) and \( J(3p, 4s) = 0.47 \).
EXCHANGE POLARIZATION OF THE 3d-SHELL AND ISOTOPE SHIFT

7 d, ..., oo d are taken into account. Then the value of equation (10) increases to an estimated value of 4.2 mK.

5. Numerical calculations of the orbitals 4s, 4d, 5d, 6d. — Sets of radial eigenfunctions are given for the Cu II: 1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹⁰ configuration by Hartee [10] and Synek [8]. The functions \( P(4s), P(4d), P(5d), P(6d) \) are to be constructed within a potential which roughly agrees with the self-consistent potential of the quoted configuration. One proceeds as follows. One 3d electron is dropped and from the remaining \( 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁹ \) electrons the central potential \( Y(r)/r \) is calculated. From this potential the function \( P(nl, r) \) was obtained as a solution of the wave equation

\[
\left[ \frac{d^2}{dr^2} + \frac{2}{r} Y(r) - \varepsilon_{nl} - \frac{l(l + 1)}{r^2} \right] P(nl, r) = 0
\]

(11)

where the normalizing condition

\[
\int_0^\infty P^2(nl, r) \, dr = 1
\]

(12)

was obeyed. Though the exchange interaction was neglected throughout this procedure the agreement of the \( P(3s, r) \) given by Hartree [10] and that one of our calculation was satisfactory. This demonstrates that \( P(3s, r) \) is very weakly affected by exchange interaction. Using the same potential the function \( P(4s, r) \) was calculated and normalized.

This procedure fails with respect to the d functions. The 3d function cannot be reproduced within the potential \( Y(r)/r \) because the potential is compensated by the centrifugal barrier over a long range. Therefore exchange interaction plays the dominant role. This difficulty was overcome in the following way [11]. The operator

\[
\frac{d^2}{dr^2} - \frac{\varepsilon_{3d} - \frac{6}{r^2}}{r^2}
\]

(13)

was applied to Hartree’s 3d function. The resultant function is divided by the 3d function itself thus providing an effective potential. Within this potential the 3d-function can be reproduced exactly. This potential served for the calculation of the higher \( nd \)-functions which thus become orthogonal to each other. These functions served for the calculation of the Slater integrals and the Vinti integrals along with Hartree’s \( 2p, 3p \) and \( 3d \) functions.

Acknowledgements. — Thanks should be given to professor W. Walcher for the sponsorship of this work and to Monsieur J. Bauche, Bellevue, for valuable advices.

References