

## Atomic Energy Levels for the Approximate ThomasFermi Potential

T. Tietz

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Written by Edgar McCarvill, 14 July 2012 19:59

The order of relative basicity in the methyl benzenes is in agreement with theoretical expectations and also with the results of previous work.<sup>4,5</sup> For the ethyl benzenes the same order is observed. However *Et*<sub>6</sub>*Bz* now occupies a much more realistic position in being slightly less basic than *Me*<sub>6</sub>*Bz* but more basic than 1245 *Me*<sub>4</sub>*Bz*. Steric factors have been proposed to account for the anomalous position of *Et*<sub>6</sub>*Bz* in its complexes with I<sub>2</sub><sup>6</sup> and ICl.<sup>7</sup>

TABLE I.  $\nu$  HCl (extrapolated to infinite dilution of aromatic in CCl<sub>4</sub>).

<i>R</i> = <i>H</i>	<i>Me</i>	<i>Et</i>	<i>iPr</i>	<i>tBu</i>
<i>R Bz</i> 2765	2735	2754	2751	2743
13 <i>R<sub>3</sub>Bz</i>	2733 <sup>a</sup>		2730	
135 <i>R<sub>3</sub>Bz</i>	2718 <sup>a</sup>	2732	2728	2720
1245 <i>R<sub>4</sub>Bz</i>	2725			
<i>R<sub>5</sub>Bz</i>	2692			
<i>R<sub>6</sub>Bz</i>	2683	2702		

<sup>a</sup> Interference by aromatic band.

Because of the smallness and the accessibility of the H atom in HCl it is believed that the steric inhibition to complex formation is either nonexistent or very small. The same arguments apply to the *iPr* and *tBu* benzenes.

With substituted side chains the order of basicity reported here is

$$Me > Et \sim iPr < tBu (\sim Me).$$

This is to be expected on theoretical grounds where the balancing of the increasing inductive effect in the above series, and the decreasing hyperconjugation effect leads to a minimum basicity between *Et* and *iPr*.<sup>8</sup> Hammett's  $\sigma$  values<sup>9</sup> also confirm this order. The same order is also followed by the 135 *Alk<sub>3</sub>Bz*.

Several authors have shown, in accordance with Mulliken's theories<sup>10</sup> that the strength of donor-acceptor complexes can be correlated with the ionization potential of the donor. For the higher *Me<sub>n</sub>Bz* no I.P.s have been experimentally determined. However they have been calculated by Franklin.<sup>11</sup> Using these values together with the experimentally determined values of the lower *Me<sub>n</sub>Bz*<sup>12</sup> a surprisingly good linear correlation exists between the I.P. and  $\nu_{HCl}$ .

These and other implications will be discussed more fully in a later publication where it is hoped to present additional higher resolution data from grating spectrometer measurements.

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## Atomic Energy Levels for the Approximate Thomas-Fermi Potential

T. TIETZ

Department of Theoretical Physics, University of Łódź, Łódź, Poland

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IN this paper we show that one can solve the Schrödinger equation for the approximate potential of Thomas-Fermi proposed by the author.<sup>1</sup> The Schrödinger equation in our case in atomic units is<sup>2</sup>

$$\frac{d^2\Phi}{dr^2} + \frac{2}{r} \frac{d\Phi}{dr} + \left[ -\epsilon^2 + \frac{2Z}{r(1+Ar)^2} - \frac{l(l+1)}{r^2} \right] \Phi = 0 \quad (1)$$

$$A = 0.643Z^{\frac{1}{3}}; \quad \epsilon = (-2E)^{\frac{1}{2}}; \quad E < 0.$$

First we write the radial wave function as

$$\Phi(r) = r^l V^{-\epsilon r} (1+t)^p g(t); \quad p = \frac{1}{2} - \frac{1}{2}(1+8\beta)^{\frac{1}{2}},$$

where

$$t = A \cdot r; \quad \beta = Z/A; \quad \alpha = \epsilon/A; \quad (2)$$

then the differential equation for *g* is

$$\frac{d^2g}{dt^2} + \left[ \frac{2p}{(1+t)} - 2\alpha + \frac{2(l+1)}{t} \right] \frac{dg}{dt} + \left[ -\frac{2p\alpha}{(1+t)} - \frac{2(l+1)\alpha}{t} + \frac{2\beta+2(l+1)p}{t(1+t)} \right] g = 0. \quad (3)$$

We can expand the eigensolutions of Eq. (3) in confluent hypergeometric polynomials

$$g = \sum_{v=0}^{\infty} c_v {}_1F_1(-v, 2l+2, 2\alpha t). \quad (4)$$

Using<sup>3</sup> the recurrence formulas for the *1F<sub>1</sub>* functions it is found

$$c_{v+1}(v+1)(v+l+2-p)/2 + c_v[\beta - (v+l+1) \cdot (v+l+1+\alpha)] + c_{v-1}(v+p+l)(v+2l+1)/2 = 0; \quad c_{-1} \equiv 0. \quad (5)$$

Since (5) is three-term recurrence relation for the *c<sub>v</sub>*, then with obvious modifications we may apply the method used by Kerner.<sup>4</sup> As zeroth approximation ( $\alpha_0$  or  $\epsilon_0$ ) and first approximation ( $\alpha_1$  or  $\epsilon_1$ ) we find

$$\epsilon_0 = Z/n - An; \quad \epsilon_1 = Z/n - nA + \frac{A^2(n+l+1)(n-l)(n+p)(n+1-p)}{4n \cdot Z/n + (n+1)A} - \frac{A^2(n+l)(n-l-1)(n+p-1)(n-p)}{4n \cdot Z/n + (n-1)A}, \quad (6)$$

where *n* is the principal quantum number. Equation (6) gives us the approximate eigenvalues  $\epsilon$ . In our case we can calculate the eigenvalues  $\epsilon$  with arbitrary accuracy. First we write (5) as

$$c_{v-1}d_{v,v-1} + c_v d_{v,v} + c_{v+1} = 0$$

$$d_{v,v} = \frac{2[\beta - (v+l+1)(\alpha + v+l+1)]}{(v+1)(v+l+2-p)} \quad (7)$$

$$d_{v,v-1} = \frac{(2l+v+1)(v+p+l)}{(v+1)(v+l+2-p)}.$$

For the self-consistency of the first Eq. (7) the determinant of the coefficients of the *c<sub>v</sub>* must be zero.

$$\Delta(\alpha) = \begin{vmatrix} d_{0,0} & 1 & 0 & \cdots & \cdots & \cdots & \cdots \\ d_{1,0} & d_{1,1} & 1 & 0 & \cdots & \cdots & \cdots \\ 0 & d_{2,1} & d_{2,2} & 1 & 0 & \cdots & \cdots \\ \cdots & \cdots & d_{m,m-1} & d_{m,m} & 1 & 0 & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{vmatrix} = 0. \quad (8)$$

The determinant (*m*+1)-th order is

$$\Delta_{m+1} = d_{m,m} \Delta_m - d_{m,m-1} \Delta_{m-1}. \quad (9)$$

Formula (9) with the convention  $\Delta_0 = 1$  and  $\Delta_1 = d_{0,0}$  permits us the computation of the determinants  $\Delta_m$  up to any order desired. The variations of (9) in our case is

$$\delta \Delta_{m+1} = \Delta_m \delta d_{m,m} + d_{m,m} \delta \Delta_m - d_{m,m-1} \delta \Delta_{m-1}$$

$$\frac{\delta d_{m,m}}{\delta \alpha} = -\frac{2(l+m+1)}{(m+1)(m+l+2-p)}. \quad (10)$$

For sufficiently large *m* we can require that

$$\Delta_{m+1}(\alpha + \delta \alpha) = \Delta_{m+1}(\alpha) + \frac{\delta \Delta_{m+1}}{\delta \alpha} \delta \alpha = 0. \quad (11)$$

The last formula (11) determines us a correction to the known approximate root  $\alpha$  of  $\Delta$ . In Kerner's<sup>4</sup> paper we have an example of calculation of eigenvalues and expansion coefficients *c<sub>v</sub>* with this method. From Eqs. (5) and (9) it follows that

$$c_v = (-1)^v \Delta_v, \quad (12)$$

TABLE I. Comparison of eigenvalues of  $\epsilon$  for  $Z=80$ .

$n$	1	Hartree	From Eq. (6)	From infinite determinant
1.	S.	74.48	74.73	74.68
2.	S.	30.41	30.88	30.49
2.	P.	29.87	30.35	30.00
3.	S.	14.76	15.23	14.42
3.	P.	14.19	14.62	13.86
3.	D.	13.08	13.71	12.66
4.	D.	5.27	6.08	4.85
4.	F.	3.09	4.64	2.55

TABLE II. Comparison of eigenvalues of  $\epsilon$  for  $Z=29$ .

$n$	1	Hartree	Hartree-Fock	Slater	Dirac	Latter	From infinite determinant
1.	S.	25.65	25.66	25.85	25.62	25.04	25.34
2.	S.	8.86	9.07	9.02	8.81	8.51	8.43
2.	P.	8.36	8.48	8.54	8.28	7.92	7.86
3.	S.	3.00	3.26	3.37	3.15	2.94	2.60
3.	P.	2.47	2.70	2.90	2.64	2.40	2.10

hence the calculation may be performed directly with the expansion coefficients  $c_p$ . In Tables I and II we have some data of our results compared with the results of other authors.<sup>5</sup> Since our approximate potential is more accurate than that of Kerner, we may expect better results. More details will be given in a forthcoming note.

The author expresses many thanks to Professor F. J. Wisniewski for many helpful discussions.

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## Ion-Molecule Reactions in Radiation Chemistry\*

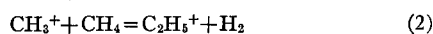
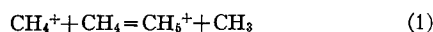
G. G. MEISELS,† W. H. HAMILL, AND R. R. WILLIAMS, JR.‡

Department of Chemistry, University of Notre Dame,  
Notre Dame, Indiana

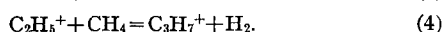
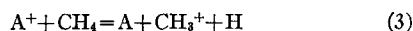
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IN early studies of radiation chemistry Lind and his collaborators<sup>1</sup> suggested that the essential steps in many cases appeared to be the reactions of positive ions with stable molecules. Recent mass spectrometric investigations by Schissler and Stevenson<sup>2</sup> have shown that a wide variety of such reactions can be directly observed and have re-emphasized their importance in radiation chemistry. We have investigated the radiolysis of methane in rare gas atmospheres and find that ion-molecule reactions offer the key to interpretation of our results.

We have used a C.E.C. 21-103 A mass spectrometer to verify the processes



previously reported<sup>2-4</sup> and to find, in addition, the processes



The major products of alpha-ray induced decomposition of methane are hydrogen, ethane, and propane.<sup>1</sup> Using 50-kv x-rays or 1.5-Mev electrons on rare gases with added methane we find these products as well as small amounts of higher alkanes as

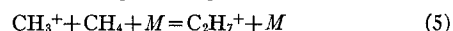
TABLE I. Electron bombardment of methane in rare gases.

Rare gas, ca 400 mm; CH <sub>4</sub> , ca 10 mm; all yields relative to H <sub>2</sub> =100	Product	A-CH <sub>4</sub>	A-CH <sub>4</sub> -I <sub>2</sub> <sup>a</sup>	Kr-CH <sub>4</sub> -I <sub>2</sub> <sup>a</sup>
H <sub>2</sub>	100	100	100	100
C <sub>2</sub> H <sub>6</sub>	45	0.6	0.1	0.1
C <sub>2</sub> H <sub>4</sub>	7	0.0	0.1	0.1
C <sub>2</sub> H <sub>10</sub>	3.5	0.0	...	...
C <sub>2</sub> H <sub>8</sub>	0.5	14.4	...	...
CH <sub>3</sub> I	...	34	200	...
C <sub>2</sub> H <sub>5</sub> I	...	18	3	...
CH <sub>2</sub> I <sub>2</sub>	...	9	25	...

<sup>a</sup> I<sub>2</sub>, ca 0.8 mm.

shown in Table I. With large amounts of added deuterium, formation of nonequilibrium amounts of both H<sub>2</sub> and HD indicates formation of both molecular and atomic hydrogen from the methane. With added iodine there is little CH<sub>2</sub>I<sub>2</sub> (see Table I) indicating that CH<sub>2</sub> radicals are not important and that H<sub>2</sub> is formed by an intermolecular process. The results with added iodine also demonstrate that higher alkanes, alkenes and alkyl radicals do not have radical precursors. These facts are consistent with steps (2), (3), and (4) above. With argon as the major component CH<sub>4</sub><sup>+</sup> and CH<sub>5</sub><sup>+</sup> should be unimportant. The appearance of ethylene in the presence of iodine suggests that it is an important intermediate which in the absence of iodine is consumed by hydrogen atoms and radicals to form higher alkanes.

Our measured  $M/N$  for molecular hydrogen in the absence of iodine approximates unity which indicates that most of the reaction chains end with step (2) and do not include step (4). Since these ion-molecule reactions have very large cross sections<sup>2</sup> it is necessary to invoke competitive processes not susceptible to mass-spectrometric observation. A plausible process is



since ethane would be expected to have a large proton affinity. At moderate pressures such three-body processes would be efficient by virtue of the long range ion-induced dipole forces. Step (5) as opposed to step (2) would stop the chain and neutralization of C<sub>2</sub>H<sub>7</sub><sup>+</sup> might readily give H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> or C<sub>2</sub>H<sub>4</sub> and H.

Experiments with krypton and methane (Table I) evidently obey a different mechanism. Since Kr<sup>+</sup> can, energetically, yield CH<sub>4</sub><sup>+</sup> but not CH<sub>5</sub><sup>+</sup>, step (1) should occur and apparently neutralization of CH<sub>5</sub><sup>+</sup> gives chiefly CH<sub>3</sub> and H<sub>2</sub>.

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† Present address: Gulf Research Corporation, Pittsburgh, Pennsylvania.

‡ Present address: Department of Chemistry, Haverford College, Haverford, Pennsylvania.

<sup>1</sup> For example, S. C. Lind and D. C. Bardwell, *J. Am. Chem. Soc.* **48**, 2335 (1926).

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## Hydrogen Bonding by NMR

A. D. COHEN AND C. REID

Department of Chemistry, University of British Columbia,  
Vancouver, Canada

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WE have measured the limiting "isolated" molecule positions to which the proton signals from alcohols and aldehydes converge as hydrogen bonding is broken down by increasing dilution with an inert solvent. The results, expressed in cycles from a cyclohexane marker, shifts to high field being called +, are given in Table I. All measurements are at a fixed frequency of 40 mc.

The dilution shifts undergone by the hydrogen bonded protons are very large (ca 200 cycles) and result in the hydroxyl protons