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Application of Variation Perturbation Theory to Some One-Center Problems of Quantum Chemistry

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Pseudo-neon molecules and pseudo-krypton complexes are discussed in the light of a recently reported theorem. It turns out that the total energy is at a minimum for smallest screening of the nuclear charge of the central atom. Both models lead to reasonable values for the ligand to central atom distance. The description of the binding in the pseudo-krypton complexes is reminiscent of the well known concept of Sidgwick.

Pseudo-Neonmoleküle und Pseudo-Kryptonkomplexe werden vom Standpunkt eines kürzlich mitgeteilten Theorems diskutiert. Es stellt sich heraus, daß die Gesamtenergie dann ein Minimum erreicht, wenn die Abschirmung der Kernladung des Zentralatoms am kleinsten ist. Beide Modelle führen zu vernünftigen Werten für den Zentralatom-Ligandenabstand. Die Beschreibung der Bindungsverhältnisse in den Pseudo-Kryptonkomplexen erinnert an frühere Vorstellungen von Sidgwick.

Des molécules du type pseudo-néon et des complexes du type pseudo-krypton sont étudiés du point de vue d'un théorème récemment publié. Il apparaît que l'énergie totale est minimale pour le plus faible effet d'écran sur la charge nucléaire de l'atome central. Les deux modèles conduisent à des valeurs raisonnables de la distance entre le ligand et l'atome central. La description de la liaison dans les complexes pseudo-krypton rappelle le concept bien connu de Sidgwick.

A. Introduction

As is well known the Variation Method of Quantum Chemistry proceeds by first finding the integral* $\langle \Psi | \boldsymbol{H} | \Psi \rangle$ and then minimizing it with respect to parameters such as Z^* (representative of the effective nuclear charges) and R (representative of the atomic distances). Furthermore, it is well known that the virial theorem $E_M = -\overline{T}_M$ is satisfied at the point (Z^*_M, R_M) of the (hyper-) surface $E = E(Z^*, R)$, where the minimum of energy $E_M = E(Z^*_M, R_M)$ is achieved, provided the kinetic energy part of the Hamiltonian $\boldsymbol{H}$ is homogeneous of the order -2 and the potential energy homogeneous of the order -1. The very fact that the virial theorem is satisfied does, however, not necessarily guarantee that E_M is close to the true energy. This depends to a large extent upon how good a trial function Ψ was chosen in the first place. If now in the sense of perturbation theory $\boldsymbol{H}^0$ is a good approximation to the Hamiltonian in question and if we know a solution Ψ^0 of the unperturbed problem, than it might be a good idea to use Ψ^0 as a trial function. It is with this understanding that we use the term Variation Perturbation Theory. Kellner [1], in his calculation (1927) of the energy of the He-ground state was probably the first to apply such a theory.

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* Assuming the trial function Ψ to be normalized.

Let the Hamiltonian $\boldsymbol{H}$ be partitioned into $\boldsymbol{H} = \boldsymbol{H}^0 + \boldsymbol{H}^1$. It then follows from what we have stated earlier that

$$\begin{aligned} E(Z^*, R) &= \langle \Psi^0 \mid \boldsymbol{H} \mid \Psi^0 \rangle \\ &= \langle \Psi^0 \mid \boldsymbol{H}^0 \mid \Psi^0 \rangle + \langle \Psi^0 \mid \boldsymbol{H}^1 \mid \Psi^0 \rangle \\ &= E^0(Z^*, R) + E^1(Z^*, R) . \end{aligned} \tag{1}$$

It has recently been shown [2] that for a certain class of problems the correction term E^1 vanishes identically if the total energy is minimized, i.e.,

$$E^1(Z^*_M, R_M) = 0$$

and, therefore,

$$E_M = E(Z^*_M, R_M) = E^0(Z^*_M, R_M) .$$

In the above mentioned paper the class of problems is defined by the Hamiltonian of a one-center problem, i.e., either a genuine atomic problem or the problem of an atom (ion) surrounded by charges q_k at distances R_k.

In the case of a genuine atomic problem E^1 is a function of the effective charge Z^* only and the value Z^*_M of this parameter at the minimum of the total energy is given implicitly by the equation $E^1(Z^*) = 0$. Besides this equation leads to the interesting conclusion [3] that for the minimum the repulsion among the electrons and the attraction between the screened charge $(Z - Z^*)$ of the nucleus and the electrons exactly balance each other [cf. Eq. (6) of the above mentioned paper]. Furthermore, if one minimizes the average energy of an atomic configuration $(nl)^m$ one obtains [3] an analytical expression for Slater's screening constants σ_{nl} for equivalent electrons. It turns out that σ_{nl} is essentially the average repulsion of two equivalent electrons multiplied by a factor $\frac{n^2}{2}$.

As pointed out already in [2] in the more general case of an atom (ion) surrounded by point charges E^1, besides being dependent upon Z^*, is also a function of q_k and R_k. As will be seen below from $E^1(Z^*, q_k, R_k) = 0$ it then follows, that the screening number σ is no longer a constant as in the atomic case but a function of the q_k and R_k. In what follows we shall consider molecules which may be treated as pseudo-atom problems and which therefore belong to the above mentioned class of problems.

B. Pseudo-Neon Molecules*

Although in principle all hydrides of second row elements with a total number of 10 electrons could be considered here we shall concern ourselves only with the case of the tetrahedral molecules BH_4^-, CH_4 and NH_4^+. These molecules have been treated by Hartmann and Gliemann [4] and by Grein [5] respectively as pseudoneon problems. If one assumes, that the nucleus is completely screened by the two 1*s*-electrons, then, the Hamiltonian for the model is

$$\boldsymbol{H} = \sum_{i=1}^{8} \left(t_i - \frac{Z-2}{r_i} \right) + \sum_{i<j}\sum \frac{1}{r_{ij}} - \sum_{i=1}^{8} \sum_{k=1}^{4} \frac{1}{r_{ik}} + \frac{4}{R}(Z-2) + \frac{1}{R}\frac{3}{2}\sqrt{6}$$
$$(q_k = 1, R_k = R) . \tag{2}$$

If it is so partitioned into $\boldsymbol{H} = \boldsymbol{H}^0 + \boldsymbol{H}^1$ that

$$\boldsymbol{H}^0 = \sum_{i=1}^{8} \left(t_i - \frac{Z^*}{r_i} \right) \tag{3}$$

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* Unpublished results, Frankfurt (Main) 1962.

and

$$\boldsymbol{H}^1 = -\sum_{i=1}^{8} \frac{Z-2-Z^*}{r_i} + \sum_{i<j}\sum \frac{1}{r_{ij}} - \sum_{i=1}^{8}\sum_{k=1}^{4} \frac{1}{r_{ik}} + \frac{4}{R}(Z-2) + \frac{1}{R}\frac{3}{2}\sqrt{6} \qquad (4)$$

then the trial function is a neon-like determinantal function

$$\Psi^0(Z^*) = |\, 2s\,\overline{2s}\,2p_0\,\overline{2p}_0\,2p_1\,\overline{2p}_1\,2p_{-1}\,\overline{2p}_{-1}\rangle \qquad (5)$$

and the theorem from [2] applies*.

$$E^1 = -8\frac{Z^*}{4}(Z-2-Z^*) + \frac{581}{128}Z^* - 32\frac{1}{R}y(x) + \frac{4}{R}(Z-2) + \frac{1}{R}\frac{3\sqrt{6}}{2}, \qquad (6)$$

where

$$y(x) = 1 - e^{-x}\left(1 + \frac{3}{4}x + \frac{1}{4}x^2 + \frac{1}{16}x^3\right),\ x = R\cdot Z^*\,.$$

R is measured in atomic units. The first term on the left side of (6) is the attraction between the "screening charge" $(Z-2-Z^*)$ and the 8 electrons of the filled $(2s,\,p)$-shell. The second term is the electron repulsion and the third represents the attraction between the 4 protons and the electrons. The fourth and the last term take account of the repulsion between the core $(Z-2)$ and the protons and among the protons respectively. Because of $E = E^0$ and $E^0 = -\overline{T}^0 = -\overline{T}$ the virial theorem is satisfied for all $Z^* = Z^*(x)$ which obey $E^1 = 0$, i.e., when all contributions add up to zero. Introduction of the screening number $\sigma = Z - 2 - Z^*$ and division of $E^1 = 0$ by $2\,Z^*$ yields

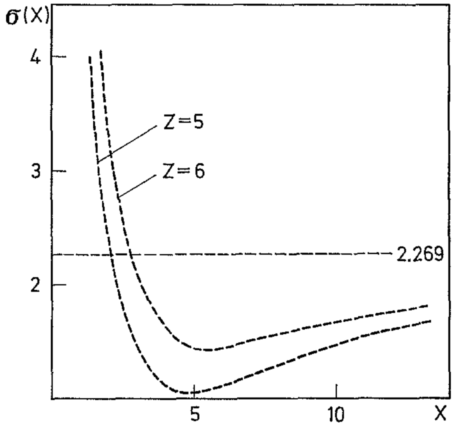

Fig. 1. Screening of the central atom charge in pseudo-neon molecules

$$\sigma(x) = \frac{581}{256} - 16\frac{y(x)}{x} + \frac{2}{x}(Z-2) + \frac{1}{x}\frac{3\sqrt{6}}{4}\,. \qquad (7)$$

This relationship is shown in Fig. 1 for $Z = 5$ (B), 6 (C). As stated earlier the screening number is no longer a constant as in the case of a free atom (ion) but

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* That the perturbation energy vanishes has been shown by Grein [6] for the energy expressions which occurred in his calculations of CH_5^+, CH_5^- and CH_5. Earlier, due to numerical inaccuracies, it had been assumed [7] that it was small. However, general conditions under which the perturbation energy necessarily vanishes have been given in [2].

Table 1. *Minimum Values for Tetrahedral s^2p^2-Hydrides*

	BH_4^-	CH_4	NH_4^+
σ_M	1.042	1.423	1.753
x_M	4.906	5.635	6.506
Z_M^*	1.958	2.577	3.247
R_M	2.506	2.187	2.004

depends upon x and, therefore, upon R. However, for $R \to \infty$ only the first term, arising from the screening of the seven "other" ($2s$, p)-electrons of the Ne-like ion equal to $\frac{581}{246} = 2.269$, remains. Although for the entire curve the virial theorem is satisfied, only one point of it corresponds to the minimum of the energy: the point of minimum screening number or maximum Z^*. This is because the total energy E is simply equal to $-\overline{T}^0 = -Z^{*2}$ along the entire curve. It is worth mentioning that only for pseudo-atom problems is the total energy at a minimum for smallest screening. For genuine molecular problems these two points do not generally coincide. Table 1 lists the values σ_M and x_M for the three molecules.

The values Z_M^* (from σ_M) and R_M (from x_M and Z_M^*) and, therefore, also the energy values, agree with the results of the earlier authors [4, 5].

From (7) it is obvious, that repulsive terms (positive) increase σ, whereas the (negative) attraction between the protons and the electrons decrease $\sigma \cdot \sigma_M$, therefore, increases from BH_4^- to NH_4^+, but not enough to compensate for the higher nuclear charge. As a result, Z_M^* and, therefore, the "binding energy" increase in the same direction. The same argument applies to the isoelectronic series CH_3^-, NH_3, OH_3^+ (compare [8]).

Since these molecules can also be treated as pseudo-neon problems their total energy is also equal to $-Z_M^{*2}$, only that Z_M^* because there are now three protons instead of four is to be determined from a somewhat different Eq. (7). This is also true for the radical CH_5^+ [9] and for the discussion of alternative lattice types of the Be_2C crystal [10]. As stated in [2], the theorem can also be applied to open shell problems such as CH_5, which has been treated as a pseudo-sodium problem [11]. In this case $E_M = -\frac{19}{18} Z_M^{*2}$.

C. Pseudo-Krypton Complexes*

The concept of the extraordinary stability of rare gas-like molecules has also been applied to coordination compounds. According to Sidgwick the great stability of the $[Co(NH_3)_6]^{3+}$-ion for example is due to the circumstance, that the complex ion resembles the closed shell structure of krypton. It is, therefore, interesting to find out whether a pseudo-krypton model predicts reasonable values for the distance between the central ion and the ligands in ammines of d^6-central ions.

We assume that the nucleus is completely screened by the 18 electrons in the $1s$, $2s$, $2p$, $3s$ and $3p$-shells. If the ligands altogether donate 12 electrons, the central ion achieves the configuration ($3d^{10}\,4s^2\,4p^6$). The ligands represent point charges of two units. The Hamiltonian for the model then is

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* Presented at the Symposium on Theoretical Chemistry, Vienna, 29. 3. – 1. 4. 1967.

$$\boldsymbol{H}=\sum_{i=1}^{18}\left(t_i-\frac{Z-18}{r_i}\right)+\sum_{i<j}\sum\frac{1}{r_{ij}}-\sum_{i=1}^{18}\sum_{k=1}^{6}\frac{1}{r_{ik}}+\frac{12}{R}(Z-18)+\frac{6}{R}(1+4\sqrt{2}) \tag{8}$$
$$(q_k=2,\ R_k=R)\,.$$

If now $\boldsymbol{H}$ is so partitioned into $\boldsymbol{H}=\boldsymbol{H}^0+\boldsymbol{H}^1$ that

$$\boldsymbol{H}^0=\sum_{i=1}^{18}\left(t_i-\frac{Z^*}{r_i}\right) \tag{9}$$

and

$$\boldsymbol{H}^1=-\sum_{i=1}^{18}\frac{Z-18-Z^*}{r_i}+\sum_{i<j}\sum\frac{1}{r_{ij}}-\sum_{i=1}^{18}\sum_{k=1}^{6}\frac{1}{r_{ik}}+\frac{12}{R}(Z-18)+\frac{6}{R}(1+4\sqrt{2}) \tag{10}$$

then the trial function is a krypton-like determinantal function

$$\Psi^0(Z^*)=|\,3d_0\,\overline{3d}_0\ldots\ldots\ldots 4s\,\overline{4s}\,4p_0\,\overline{4p}_0\ldots\rangle \tag{11}$$

and we may again apply the theorem from [2].

$$E^1=V_{\sigma e}+V_{ee}+V_{le}+V_{lc}+V_{ll}\,. \tag{12}$$

The attraction between the screening charge $\sigma=Z-18-Z^*$ and the 18 $3d$, $4s$, $4p$-electrons is

$$V_{\sigma e}=-\sigma\left(10\frac{Z^*}{9}+2\frac{Z^*}{16}+6\frac{Z^*}{16}\right)=-\frac{29}{18}Z^*\sigma\,.$$

The repulsion among the 18 electrons is

$$\begin{aligned}V_{ee}&=45\,E_{av}(3d^2)+E_{av}(4s^2)+15\,E_{av}(4p^2)\\&+12\,E_{av}(4s\,4p)+20\,E_{av}(4s\,3d)+60\,E_{av}(4p\,3d)\,.\end{aligned}$$

The average energies E_{av} for pairs of equivalent as well as nonequivalent electrons have been listed in [12] in terms of the well kown Slater-Condon parameters. These have been calculated by HÜRTHLE [13], using hydrogen-like functions. One then finally obtains

$$V_{ee}=8.622\,Z^*\,.$$

The attraction between the 18 electrons and the 6 ligands is

$$V_{le}=-120\,J_{32}-24\,J_{40}-72\,J_{41}\,,$$

where the relevant integrals $J_{nl}=(\mathcal{R}_{nl}\frac{1}{r_>}\mathcal{R}_{nl})$ are

$$J_{32}=\frac{1}{R}\left\{1-e^{-{}^2\!/_3x}\left(1+\frac{5}{9}x+\frac{4}{27}x^2+\frac{2}{81}x^3+\frac{2}{729}x^4+\frac{2}{10935}x^5\right)\right\}$$

$$J_{40}=\frac{1}{R}\Bigl\{1-e^{-{}^1\!/_2x}$$
$$\times\left(1+\frac{7}{16}x+\frac{3}{32}x^2+\frac{3}{128}x^3-\frac{1}{256}x^4+\frac{3}{2048}x^5-\frac{5}{36864}x^6+\frac{1}{147456}x^7\right)\Bigr\}$$

$$J_{41}=\frac{1}{R}\Bigl\{1-e^{-{}^1\!/_2x}$$
$$\times\left(1+\frac{7}{16}x+\frac{3}{32}x^2+\frac{5}{384}x^3+\frac{1}{768}x^4+\frac{13}{30720}x^5-\frac{1}{20480}x^6+\frac{1}{245760}x^7\right)\Bigr\}\,.$$

The repulsion between the core $(Z-18)$ and the 6 ligands is simply

$$V_{lc}=\frac{12}{R}(Z-18)$$

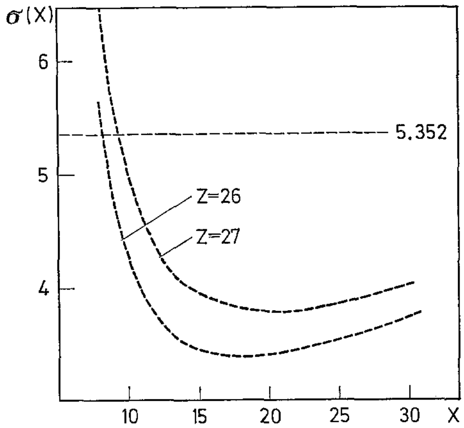

Fig. 2. Screening of the central ion charge in pseudo-kryton complexes

and the repulsion between the ligands in octahedral positions is given by

$$V_{ll} = \frac{6}{R}(1 + 4\sqrt{2}) = 39.941\frac{1}{R}.$$

Division of $E^1 = 0$ by $\frac{29}{18}Z^*$ leads to

$$\sigma(x) = 5.3516 - 74.4828\frac{y_1(x)}{x} - 59.5862\frac{y_2(x)}{x} + \frac{1}{x}[24.7909 + 7.4483\,(Z - 18)], \tag{13}$$

where

$$y_1(x) = 1 - e^{-{}^2\!/_3 x}\left(1 + \frac{5}{9}x + \frac{24}{7}x^2 + \frac{2}{81}x^3 + \frac{2}{729}x^4 + \frac{2}{10935}x^5\right)$$

$$y_2(x) = 1 - e^{-{}^1\!/_2 x}\left(1 + \frac{7}{16}x + \frac{3}{32}x^2 + \frac{1}{64}x^3 + \frac{7}{10240}x^5 - \frac{13}{184320}x^6 + \frac{7}{1474560}x^7\right).$$

Eq. (13) is illustrated in Fig. 2 for $Z = 26$ (Fe), 27 (Co). Table 2 lists the values σ_M and x_M for the energy minimum*, as well as the corresponding values Z^*_M, R_M.

Table 2. *Minimum Values for d^6-Hexammines*

	Fe(II)	Co(III)	Ni(IV)
σ_M	3.399	3.774	4.113
x_M	18.679	20.993	22.930
Z^*_M	4.601	5.226	5.887
R_M	4.059	4.017	3.895

The energy in all three cases is equal to $E_M = -\frac{29}{36}Z^{*2}_M$.

It turns out that the pseudo-krypton model predicts reasonable metal-ligand distances. The effective radius of NH_3 in transition metal ammines is known to be

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* I am indebted to Dipl. Phys. E. Frenkel for the numerical evaluation of Eqs. (7) and (13).

1.40 Å from crystallographic data [14]. Using the Goldschmidt radii for Fe(II) and Co(III) one then gets 4.21 and 3.88 atomic units respectively for the ligand to central ion distances in the Fe(II) and Co(III)-hexammines. The first figure corresponds to the (quintet) groundstate of the $[Fe(NH_3)_6]^{2+}$-ion. In the excited $^1A_1$-state one would expect the distance to be even smaller.

D. Discussion

The models with which we have been concerned here only lead to binding with respect to the ionic components from which they are built up, i.e. with respect to C^{4-} and $4\,H^+$ in the case of CH_4. They do not lead to binding with respect to the neutral components. They are really only limiting structures which would have to be included in a VB-type treatment, It is, therefore, remarkable, that they, nonetheless, lead to atomic distances which are not far from reality.

Furthermore it is interesting to compare the effective charge Z^* in the compounds and the effective charge Z_0^*, calculated by minimizing the average energies of the free central atoms (ions) Relevant data are collected for CH_4 and $[Co(NH_3)_6]^{3+}$ in Table 3.

Table 3. *Effective Charges for the outer Electrons of the Central Atom (Ion)*

C ($2s^2\,2p^2$)	:3.085	Co^{3+} ($3d^6$)	:7.117
C^- ($2s^2\,2p^3$)	:2.753	Co^{3-} ($3d^8\,4s^1\,4p^3$)	:5.403
CH_4	:2.577	$[Co(NH_3)_6]^{3+}$	:5.226

As one would expect from the model we have used, Z^* is smaller than Z_0^* of C and Co^{3+}, respectively. However, C and Co^{3+} have not "kept all the electrons", which were given them by the model: whereas Co^{3+} has kept only 6 out of 12, C has kept only 1 or 2 out of 4. Thus the description of the binding in the hexammine-complex by a pseudo-krypton model bears a certain resemblance to the description which was proposed more than 30 years ago by Sidgwick [15] for this type of coordination compound.

References

1. Kellner, G. W.: Z. Physik **44**, 91 (1927).
2. Hansen, K. H.: Theoret. chim. Acta (Berl.) **6**, 87 (1966).
3. — Theoret. chim. Acta (Berl.) **6**, 268 (1966).
4. Hartmann, H., u. G. Gliemann: Z. physik. Chemie N.F. **15**, 108 (1958).
5. Grein, F.: Theoret. chim. Acta (Berl.) **1**, 52 (1962).
6. — Dissertation Frankfurt (Main) 1960.
7. Volpers, R.: Dissertation Frankfurt (Main) 1958.
8. Hartmann, H., u. G. Gliemann: Z. physik. Chemie N.F. **19**, 29 (1959).
9 —, u. F. Grein: Z. physik. Chemie N.F. **22**, 20 (1959).
10. —, u. W. Mosch: Theoret. chim. Acta (Berl.) **2**, 29 (1964).
11. —, F. Grein u. R. Zettler-Thieler: Z. physik. Chemie N.F. **23**, 140 (1960).
12. Slater, J. C.: Quantum theory of atomic structure, Vol. I. New York: McGraw-Hill 1960.
13. Hürthle, M.: Unpublished results.
14. Basolo, F., and R. G. Pearson: Mechanisms of inorganic reactions. New York and London: John Wiley 1958.
15. Sidgwick, N. V.: J. Amer. chem. Soc. **53**, 1367, 3225 (1931).

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