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Modelling Properties of Molecules with open d- or f-Shells Using Density Functional Theory

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Abstract: A new, non-empirical, Density Functional Theory (DFT) based Ligand Field (LF) model is proposed. The calculation involves two steps: (i) an Average Of Configuration (AOC), with equal occupation of the d- or f-orbitals is carried out, (ii) with these orbitals kept frozen, the energies of all Single Determinants (SD) within the whole LF manifold is performed. These energies are then used to estimate all the Racah- and LF-parameters needed in a conventional LF calculation. The results of this first-principle prediction are in very good agreement with the experimental values. Sample calculations of tetrahedral and octahedral Cr-complexes, hexa-acquo Ni(II)-and octa-acquo Gd(III)-complexes are used to validate the new model and to analyse the calculated parameters.

Keywords: Density functional theory · Electron paramagnetic resonance · Ligand field theory · Shielding constant · Zero field splitting

1. Introduction

Recently we presented a new model [1] based on a multi-determinantal description of the multiplet fine structure of the whole ligand field manifold. The key feature of this approach is the explicit treatment of near degeneracy correlation using *ad hoc* Configuration Interaction (CI) within the active space of Kohn-Sham (KS) orbitals with dominant d- or f-character. The calculation of the CI matrices is based on a symmetry decomposition and/or on a ligand field analysis of the energies of all single determinants (micro-states) calculated according to Density Functional Theory (DFT) for frozen KS-orbitals corresponding to the averaged configuration, eventually with fractional occupations, of the d- or f-orbitals. This procedure yields multiplet energies with an accuracy of a few hundred wave numbers and fine structure splitting accurate to less than a tenth of this amount.

Currently we are extending this procedure to the calculation of all customary molecular properties *e.g.* Zero Field Splitting (ZFS) [2], Zeeman interaction [3], Hyper-Fine Splitting (HFS) [3], magnetic exchange coupling [4], shielding constants [5], *etc.* …

2. Description of the Method

The current DFT software includes functionals at the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) levels. The former approximation is well adapted for molecular structure calculation: M–L bond lengths are usually accurate to ±0.02 Å but bond energies are too large. The latter approximation, however, is roughly twice as expensive in computer time and yields M–L bond energies accurate to ±5 kcal/mol. Recently a new generation of functionals called meta-GGA emerged. These functionals are more accurate but also more expensive and their implementation in computer codes is not yet generalized. It is generally accepted that all these functionals (LDA and GGA) describe well the so-called dynamical correlation, however, none of them includes near degeneracy correlation. In the method described here we address this problem specifically and include CI of all d- and f-orbitals of valence electrons. The calculation scheme we developed includes three steps as described below.

We assume that we know the molecular geometry, either from a first principle geometry optimisation or from X-ray data. Moreover, for the sake of simplicity, let us focus the following description to open d-shells: the extension to open f-shells is similar. The first step consists in a spin-restricted, *i.e.* same orbitals for same spin, Self Consistent Field (SCF) DFT calculation of the average of the d^n configuration (AOC), providing an equal occupation n/5 on each MO dominated by the d-orbitals. The KS-orbitals which we construct using this AOC are best suited for a treatment in which interelectronic repulsion is, as is done in LF theory, approximated by atomic-like Racah parameters B and C. The next step consists in a spin-unrestricted calculation of the manifold of all Slater Determinants (SD) originating from the d^n shell, *i.e.* 45, 120, 210, and 252 SD for $d^{2,8}$, $d^{3,7}$, $d^{4,6}$, and d^5 transition metal (TM) ions, respectively. These SD energies are used in the third step to extract the parameters of the one-electron 5×5 LF matrix $\langle i | h_{LF} | j \rangle$ as well as Racah's parameters B and C in a procedure which we describe below. Finally, we introduce these parameters as input for a LF program allowing the calculation of all the multiplets using CI of the full LF manifold utilizing the symmetry as much as

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possible. We should note that in classical LF theory, it is only the LF matrix which carries information about the symmetry and the actual bonding in the complex, thus providing useful chemical information.

In order to establish a link between ligand field theory and the energy of each SD mentioned earlier we need to introduce an effective LF Hamiltonian h_{LF}^{eff} together with its five eigenfunctions $\varphi_I\{h_{LF}^{eff}\varphi_1=\varepsilon_i\varphi_i$, i=1,…,5} which are in general linear combination of the five d-orbitals:

$$\begin{bmatrix}\varphi_1\\ \varphi_2\\ \varphi_3\\ \varphi_4\\ \varphi_5\end{bmatrix} = \mathbf{C}\cdot\begin{bmatrix}d_{x^2-y^2}\\ d_{yz}\\ d_{z^2}\\ d_{xz}\\ d_{xy}\end{bmatrix}$$

and where **C** is an orthogonal 5×5 matrix. Using this definition we can express the energy of each single determinant in terms of $\langle\varphi_i|h_{LF}^{eff}|\varphi_i\rangle$, the diagonal elements of the ligand field splitting operator and electrostatic Coulomb and Exchange integrals:

$$\begin{aligned}E\left(SD_k^{\varphi}\right) &= E\left(\det\left|\varphi_{i(k,1)}\sigma_{i(k,1)}\varphi_{i(k,2)}\sigma_{i(k,2)}\ldots\varphi_{i(k,n)}\sigma_{i(k,n)}\right|\right)\\ &= E_0+\sum_{i\in k}\left\langle\varphi_i\middle|h_{LF}^{eff}\middle|\varphi_i\right\rangle+\sum_{i<j}\left(J_{ij}-K_{ij}\delta_{\sigma_i\sigma_j}\right)\end{aligned}\qquad(1)$$

The single determinants SD_k^{φ} are labelled with the subscript μ = 1, …, $\binom{10}{n}$ and where the superscript φ refers to eigenfunctions of the ligand field Hamiltonian h_{LF}. The summation $i\in k$ of ligand field splitting matrix elements $\langle\varphi_i|h_{LF}^{eff}|\varphi_i\rangle$ specify the occupation of the level φ_i, while $J_{ij}=\langle\varphi_i\varphi_i|\varphi_j\varphi_j\rangle$ and $K_{ij}=\langle\varphi_i\varphi_j|\varphi_i\varphi_j\rangle$; σ_i are spin functions and E_0 represents the gauge origin of energy. This expression only involves $\langle\varphi_i|h_{LF}^{eff}|\varphi_i\rangle$ the diagonal matrix elements of h_{LF}^{eff}. In order to obtain $\langle\varphi_i|h_{LF}^{eff}|\varphi_i\rangle$ the full matrix representation of h_{LF}^{eff}, we make use of the general observation that the KS-orbitals and the set of SD considered in Eqn. (1) convey all the information needed to setup the LF matrix. In [1] we give a justification for this.

Thus, let us denote KS-orbitals dominated by d-functions which result from an AOC d^n DFT-SCF calculation with a column vector $\vec{V}_i$. From the components of the eigenvector matrix built up from such columns one takes only the components corresponding to the d functions. Let us denote the square matrix composed of these column vectors by **U** and introduce the overlap matrix **S**:

$$\mathbf{S}=\mathbf{U}\mathbf{U}^{T}\qquad(2)$$

Since **U** is in general not orthogonal, we use Löwdin's symmetric orthogonalisation scheme to obtain an equivalent set of orthogonal eigenvectors (**C**):

$$\mathbf{C}=\mathbf{S}^{-\frac{1}{2}}\mathbf{U}\qquad(3)$$

We identify now these vectors as the eigenfunctions of the effective LF Hamiltonian h_{LF}^{eff} we seek as

$$\varphi_i=\sum_{\mu=1}^{5}c_{\mu i}d_\mu\qquad(4)$$

Thus, the fitting procedure described in the previous section will enable us to estimate $h_{ii}=\langle\varphi_i|h_{LF}^{eff}|\varphi_i\rangle$ and hence the full representation matrix of h_{LF}^{eff} as

$$h_{\mu\nu}=\left\langle d_\mu\middle|h_{LF}^{eff}\middle|d_\nu\right\rangle=\sum_{i=1}^{5}c_{\mu i}h_{ii}c_{\nu i}\qquad(5)$$

In order to calculate the electrostatic contribution (2nd term in Eqn. (1)) it is useful to consider the transformation from the basis of SD_k^{φ} to the one of SD_μ^d. Using basic linear algebra, we get:

$$\left|SD_k^{\varphi}\right\rangle=\sum_{\mu}T_{k\mu}\left|SD_\mu^{d}\right\rangle\qquad(6)$$

where $T_{k\mu}$ = det$|c_{i(k,1:n),j(\mu,1:n)}|$ *i.e.* the determinant of a nxn sub-matrix of $\mathbf{C}\otimes\sigma$ *i.e.* the direct product between C and $\begin{bmatrix}1&0\\0&1\end{bmatrix}$.

$$\begin{vmatrix}c_{i(k,1),j(\mu,1)} & c_{i(k,1),j(\mu,2)} & \cdots & c_{i(k,1:n),j(\mu,n)}\\ c_{i(k,2),j(\mu,1)} & c_{i(k,2),j(\mu,2)} & \cdots & c_{i(k,2),j(\mu,n)}\\ \cdots & \cdots & \cdots & \cdots\\ c_{i(k,n),j(\mu,1)} & c_{i(k,n),j(\mu,2)} & \cdots & c_{i(k,n),j(\mu,n)}\end{vmatrix}$$

with the indices of the spinorbitals $\varphi_{i(k,1)}\sigma_{i(k,1)}$, $\varphi_{i(k,2)}\sigma_{i(k,2)}$, …, $\varphi_{i(k,n)}\sigma_{i(k,n)}$ and $d_{j(\mu,1)}\sigma_{j(\mu,1)}$, $d_{j(\mu,2)}\sigma_{j(\mu,2)}$, …, $d_{j(\mu,n)}\sigma_{j(\mu,n)}$ respectively. Note that these indices are in fact a two-dimensional array of (number of SD) x (number of electrons or holes) integers. Finally the energy of a SD in Eqn. (1) can be rewritten as

$$E_k=E\left(SD_k^{\varphi}\right)=\sum_i\left\langle\varphi_i\middle|h_{LF}\middle|\varphi_i\right\rangle+\sum_{\mu,\nu}T_{k\mu}T_{k\nu}\left\langle SD_\mu^{d}\middle|G\middle|SD_\nu^{d}\right\rangle\qquad(7)$$

where G =1/r$_{12}$, *i.e.* the electrostatic repulsion of all electron pairs in the LF manifold. The matrix elements are readily obtained using Slater's rules and the resulting electrostatic two-electron integrals $\langle ab|cd\rangle$ in terms of Racah's parameters.

Having obtained energy expressions for each SD_k^{φ}: $\langle\varphi_i|h_{LF}|\varphi_i\rangle$, B, C and E_0 are estimated using a least-squares procedure. Using matrix notation, we obtain an *overdetermined* system of linear Eqns. (8) with the unknown parameters stored in $\vec{X}$=(h$_{11}$, …, h$_{55}$, B, C), and given by Eqn. (9).

$$\vec{E}=A\vec{X}\qquad(8)$$

$$\vec{X}=(A^{T}A)^{-1}A^{T}\vec{E}\qquad(9)$$

It is worthwhile to note that the KS-eigenvalues ε_i^{KS} of the orbitals with dominant d-character are almost equal to the ligand field parameters obtained in the fitting procedure, *i.e.*

$$\varepsilon_i^{KS}\cong E_0+\left\langle\varphi_i\middle|h_{LF}\middle|\varphi_i\right\rangle\qquad(10)$$

Thus, we conclude this section with the statement that the separation between KS-eigenvalues of orbitals with dominant d-character are good approximations for the ligand field splitting parameters.

For cases where the fine structure is sought it is now easy to include spin-orbit coupling and calculate:

$$\left\langle SD_k^{d}\middle|\zeta_d\sum_{i=1}^{n}\ell_i\cdot s_i\middle|SD_{k'}^{d}\right\rangle\qquad(11)$$

where ζ_d is the spin orbit coupling constant whose value is easily obtained either from a ZORA calculation [6] or from the radial part of the d-orbitals as:

$$\left\langle d_\mu\middle|\zeta(\vec{r})\middle|d_\nu\right\rangle\approx k_{orb\_red}\left\langle R_{nd}\middle|r^{-3}\middle|R_{nd}\right\rangle$$

where k_{orb_red} is an orbital reduction factor equal to the population on the metal atom. Thus, properties involving spin-orbit coupling are obtained by adding Eqn. (11) to the full LF-Hamiltonian $H_0+H_{ligandfield}+H_{elect\_rep}+H_{spinorbit}$ and calculating the sought properties from its eigenfunctions.

Computational Details

All DFT calculations have been performed using the ADF program package [6]. The approximate SCF KS one-electron equations are solved by employing an expansion of the molecular orbitals in a basis set of Slater-type orbitals (STO). All atoms

Table 1. Electronic transition energies of CrX_4, X=Cl and Br, with geometries optimized using LDA functional and calculated using values of B, C and 10Dq from least square fit to DFT energies of the Slater determinants according to the method describe in section 2. Optimized geometries correspond to stable minima in the ground state potential surface with harmonic frequencies of the α_1, ε, $\tau_2(1)$ and $\tau_2(2)$ vibrational modes of 359, 113, 126, and 464 cm^{-1} (for $CrCl_4$); 207, 63, 82, and 350 cm^{-1} (for $CrBr_4$), respectively.

	Cr Cl_4			$CrBr_4$	
Term	This work	LF-fit	Exp.[a]	This work	Exp.[a]
$^3A_2(e^2)$	0	0	0	0	0
$^1E(e^2)$	6542	6089	-	6373	6666
$^1A_1(e^2)$	11114	10586	-	10698	10869
$^3T_2(e^1t_2^1)$	7008	7010	7250	6163	-
$^3T_1(e^1t_2^1)$	10316	10440	10000	9269	-
$^1T_2(e^1t_2^1)$	13454	12991	12000	12434	-
$^1T_1(e^1t_2^1)$	15074	14718	-	14037	-
$^1A_1(t_2^2)$	32099	30599	-	30120	-
$^1E(t_2^2)$	21121	20716	-	19271	-
$^3T_1(t_2^2)$	16033	16229	16666	14424	13258
$^1T_2(t_2^2)$	21217	20822	-	19373	-
R(M-X)	2.104	-	-	2.264	-
B	355	376	-	347	-
C	1903	1579	-	1855	-
10Dq	7008	7250	-	6162	-
Std Dev.	0.030	-	-	0.030	-

[a] Studer P. Thesis, University of Fribourg, **1975**.

were described through triple-ς STO basis sets given in the program database (basis set IV) and the core-orbitals up to 3p for the TM and up to 1s (for O, N, C), 2p (Cl) and 3d (Br) were kept frozen. We used the local density approximation (LDA), where exchange-correlation potential and energies have been computed according to the Vosko, Wilk and Nusair's (VWN) [7] parameterization of the electron gas data.

3. Results and Discussion

Tetrahedral d^2 CrX_4 ($X = Cl^-, Br^-$)

Tetrahedral d^2 complexes possess a $^3A_2(e^2)$ ground state as well as $^3A_2 \rightarrow {}^3T_2$ and $^3A_2 \rightarrow {}^3T_1$, $e \rightarrow t_2$ singly excited states. They give rise to broad d–d transitions in the optical spectra. In addition, spin-flip transitions within the e^2 configuration lead to sharp line excitations. Multiplet energies from LDA agree within a few hundred cm^{-1} with experimental data. In particular the $^3A_2 \rightarrow {}^3T_2$ transition energy and thus 10Dq nicely agrees with experiment as is seen from inspection of Table 1. Experimental transition energies for $CrCl_4$ and $CrBr_4$ as well as values of B, C and 10Dq deduced from a fit to experiment for $CrCl_4$ are also listed.

Octahedral Cr^{III} d^3 Complexes

In Table 2 we list the predicted (this work), adjusted (LF fit to exp.) and observed (Exp.) multiplet energies for CrX_6^{3-} ($X = F^-, Cl^-, Br^-, CN^-$) complex ions. We used a LDA functional to calculate the Cr^{III}-X bond lengths and we compare these results with energies from a LF calculation utilizing values of B, C, and 10Dq obtained from a best fit to the spectra. Bond lengths are too long while values of 10Dq are too small compared to experiment. The situation improves if instead of optimised, experimental bond lengths are taken for the calculation. Even in this case, spin-forbidden transitions come out by 3000–4000 cm^{-1} too low in energy compared to experiment. Clearly, in this example of highly charges species, our prediction is much less accurate. In order to improve the quality of the prediction we obviously need to consider the environment of the CrX_6^{3-} chromophore by adding an appropriate embedding potential to the KS-Hamiltonian. Already the use of experimental bond lengths does significantly improve the precision of our calculation as mentioned before. A full analysis of this problem is given in [8]. For the $Cr(CN)_6^{3-}$ ion we note a value of 10Dq which is by 4000 cm^{-1} higher than the experimental one. This is unusual and not expected: calculated and experimental Cr–C bond distances are indeed very close. We can conclude that for the latter system, existing DFT functionals do not perform properly. In addition the standard deviations are too high. More work is needed to better understand the phenomenon and to improve this.

Octahedral Hexaacquo Ni(II) d^8 Complexes

In Table 3 we list the multiplet energies for the $Ni(H_2O)_6^{2+}$ obtained according to the method outlined in section 2. The experimental electronic spectrum of Ni(II) ion in aqueous solution exhibit three absorption peaks centred at 8800 cm^{-1} ($^3A_2 \rightarrow {}^3T_2$), at 15000 cm^{-1} ($^3A_2 \rightarrow {}^3T_1$), and at 25500 cm^{-1} ($^3A_2 \rightarrow {}^3T_1$). The agreement with the predicted multiplets is perfect in this case.

From the spin-orbit splitting of the $^3A_2$ ground state it is possible to obtain the ZFS D-tensor using a conventional spin Hamiltonian approach

$$H_{ZFS} = \vec{S} \cdot \mathbf{D} \cdot \vec{S} = D\left(\hat{S}_z^2 - \frac{2}{3}\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right)$$

and equating the energies of the spin-orbit components of the $^3A_2$ to the eigenvalues of this spin Hamiltonian. The result is given below:

$$\begin{bmatrix} 0.0000 \\ 0.1074 \\ 0.1645 \end{bmatrix} = \begin{bmatrix} -2/3 & 0 & 1 \\ 1/3 & -1 & 1 \\ 1/3 & 1 & 1 \end{bmatrix} \begin{bmatrix} D \\ E \\ C \end{bmatrix}$$

The solution of this set of three linear equations is: D = 0.1360 cm^{-1} and E = 0.0285 cm^{-1}. The third parameter C describes the arbitrary energy origin. There are experimental measurements of the ZFS for $Ni(H_2O)_6^{++}$ in $NiSiF_6.6H_2O$ available. At 90K the ZFS is 0.17 cm^{-1}. However, D is very sensitive on alteration of the temperature and pressure. Thus, an exhaustive description of the observed ZFS needs a dynamical study of the process which goes far beyond the goal of this work.

$[Gd(H_2O)_8]^{3+}$ in the D_{4d} Symmetry

The ligand field splitting in lanthanide ions has consequences in optical and magnetic spectroscopy. In the analysis of electron paramagnetic resonance spectra of Gd^{3+} complexes, a major role is played by the Zero Field Splitting (ZFS), which is a high order consequence of the ligand field and the spin-orbit coupling. We presented a general parameterised method and a computer program for the study of the excited

Table 2. Electronic transition energies of CrX_6^{3-}, X = F^-, Cl^-, Br^-, and CN^- molecules with geometries optimized using LDA functionals calculated using values of B, C and 10Dq from least square fit to DFT energies of the Slater determinants and to experiment. The values of $(10Dq)_{orb}$ as deduced from the e_g-t_{2g} KS-orbital energy difference taken from the …$t_{2g}^{1.8}eg^{1.2}$ SCF KS-energies are also listed. Experimental transition energies are also listed.

Term	CrF_6^{3-}			$CrCl_6^{3-}$			$CrBr_6^{3-}$			$Cr(CN)_6^{3-}$		
	This work	LFT fit to exp.	Exp.	This work	LFT fit to exp.	Exp.	This work	LFT fit to exp.	Exp.	This work	LFT fit to exp.	Exp. Exp.
$^4A_{2g}(t_{2g}^3)$	0	0	0	0	0	0	0	0	0	0	0	0
$^2E_g(t_{2g}^3)$	12497	15802	16300[a]	10756	14426	14430[b]	10333	13900	13900[b]	9413	12034	12460[f]
$^2T_{1g}(t_{2g}^3)$	13044	16461	16300[a]	11180	14873	-	10694	14348	-	9682	12425	13070[f]
$^2T_{2g}(t_{2g}^3)$	18628	23260	23000[a]	15918	21037	-	15185	20281	-	15234	19084	18370[f]
$^4T_{2g}(t_{2g}^1e_g^1)$	13569	15298	15200[a]	10911	12800	12800[b]	9816	12400	12400[b]	30760	26595	26700[f]
$^4T_{1g}(t_{2g}^1e_g^1)$	19443	22262	21800[a]	15618	18198	18200[b]	13992	17700	17700[b]	35910	32743	32680[f]
$^2A_{1g}(t_{2g}^1e_g^1)$	24071	28709	-	20056	25351	-	18709	24459	-	38324	36488	-
$^2T_{1g}(t_{2g}^1e_g^1)$	26348	31473	-	21878	27421	-	20316	26503	-	40022	38569	-
$^2T_{2g}(t_{2g}^1e_g^1)$	25959	30970	-	21568	27079	-	20047	26159	-	39983	38438	-
$^2E_g(t_{2g}^1e_g^1)$	27819	33341	-	23147	29098	-	21530	28126	-	41084	39952	-
$^4T_{1g}(t_{2g}^1e_g^1)$	30339	34636	35000[a]	24375	28455	-	21861	27643	-	63147	55352	-
R(M-X)	1.957	-	1.933[c]	2.419	-	2.335[d]	2.588	-	2.47[e]	2.071	-	2.077[g]
B	605	734	-	484	550	-	427	543	-	452	554	-
C	2694	3492	-	2403	3450	-	2395	3296	-	1919	2559	-
10Dq	13598	15297	-	10911	12800	-	9816	12400	-	30760	26595	-
SD	0.113	-	-	0.105	-	-	0.113	-	-	0.105	-	-
$(10Dq)_{orb}$[h]	13928	-	-	10775	-	-	9622	-	-	30953	-	-

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states of lanthanide complexes [2]. We performed a 1st principles determination of the ZFS of the $[Gd(H_2O)_8]^{3+}$ aqua ion and the corresponding EPR peak-to-peak width in solution and we calculated the influence of the various contributions to the effective Hamiltonian on the splitting of the ground state multiplet.

If one considers the ligand field interaction, most of the states are split into 'Kramers' doublets. The $^8A_1$ ground state is split into four doublets with relative energies 0, 0.03, 0.084, and 0.142 cm^{-1}. The experimental splitting of the $^8A_1$ ground state of the Gd^{3+} aqua ion is between 0.2 and 0.5 cm^{-1} depending on the experiment, *i.e.* a result which is in good agreement with our prediction.

4. Conclusion

The model we present here is simple and easy to implement. The quality of the predictions is exceptional with regard to the low computer time consumption. Keeping in mind that Time Dependant (TD) DFT is restricted to closed shell molecules, the model presented here is probably unique in addressing excited states of molecules with open d- and f-shells. Moreover, the concepts used here (LF theory, Racah parameter) are familiar to all chemists and spectroscopists. Thus, the quantities involved in the calculations provide immediate insights and facilitates communication between theorists and experimentalists. On the basis of our results we can conclude that DFT provides a rigorous interpretation of the LF parameters and leads to a justification of the parametric structure of the classical LF theory. It is remarkable that a theory which was

Table 3. Predicted multiplet energies of $Ni(H_2O)_6^{++}$ in D_{2h} symmetry based on the five KS-orbitals with dominant metal-3d character. The fine structure (spin-orbit coupling) is also included

Degeneracy (Multiplicity)	Multiplet Energy [$10^3 cm^{-1}$]	S(S+1)	Spin-Orbit splitting [$10^3 cm^{-1}$]		
3	0.0000000	2.000	0.0000000	0.0001074	0.0001645
3	8.8252743	2.000	8.5714426	8.6014099	8.7127700
3	8.8414083	2.000	8.7298366	8.7386983	9.0699081
3	8.8737000	2.000	9.0847504	9.0917825	9.2288776
3	14.5809908	2.000	13.9177850	14.1466476	14.1493461
3	14.5921568	2.000	14.3609969	14.3613509	14.3698568
3	14.5934211	2.000	15.0584802	15.0595351	15.0618965
1	14.6214912	0.000	15.7200626		
1	14.6221451	0.000	15.7224490		
1	23.0538531	0.000	22.8226585		
1	23.0674913	0.000	22.8343287		
1	23.0966616	0.000	22.8599397		
1	23.5866071	0.000	23.7076105		
3	25.2933052	2.000	25.2187733	25.2277340	25.5319615
3	25.3050996	2.000	25.5347498	25.5451571	25.5868215
3	25.3063639	2.000	25.5873367	25.5920497	25.7705637
1	27.5214320	0.000	27.6420000		
1	27.5214702	0.000	27.6420403		
1	27.5376041	0.000	27.6580624		
1	34.1878765	0.000	34.3128908		
1	34.2156132	0.000	34.3405845		
1	34.5899024	0.000	34.7083317		
1	34.5948335	0.000	34.7133008		
1	34.6084717	0.000	34.7269772		
1	60.3671270	0.000	60.5117478		

discovered three quarter of a century ago is still modern.

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