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On the Empirical Validity of Koopmans' Theorem

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The application of Koopmans' theorem is investigated within the context of the LCAO interpretation of a general SCF formalism. An empirical criterion for the validity of the assumption of identity of corresponding orbitals in the ion and parent system is discussed. Calculations on He, Li, Be and pyridine are reported.

Die Gültigkeit von Koopmans' Theorem läßt sich mittels eines verallgemeinerten SCF-Formalismus prüfen. Ein Kriterium für das Zutreffen der Annahme, einander entsprechende Einteilchenzustände in Atom und Tochter-Ion seien identisch, wird in diesem Zusammenhang diskutiert. Die Rechnungen sind am Helium, Lithium, Beryllium und Pyridin durchgeführt worden.

La validité du théorème de Koopmans dans un formalisme SCF général est étudiée au cadre d'une interprétation LCAO. Un critère empirique pour l'identité des orbitales de l'ion et du système père correspondant est discuté. Nous rapportons des calculs sur He, Li, Be et pyridine.

Introduction

Before the introduction of the open-shell SCF formalism of Roothaan [*10*] it was necessary, in LCAO calculations, to employ Koopmans' theorem [*4*] to determine the ionization potentials of closed-shell systems, *i. e.*, to equate the ionization potential with the negative of the orbital energy of that orbital from which the electron was removed. This is not an approximation in the theoretical context if the corresponding orbitals of the ion and parent system are identical. As an approximation to the experimental value it suffers much the same fate as other calculated energy quantities.

Recently Fraga and Birss [*3*] have given the LCAO form of their SCF formalism for a general system without restrictions on the number or symmetry of open-shells. Due to its characteristics this theory is convenient for an investigation of the basis of Koopmans' theorem [*5*] and the relation between a calculated ionization potential, the corresponding orbital energy and the experimental ionization potential.

The systems used in this investigation are the helium, lithium and beryllium atoms and the pyridine molecule. Accurate SCF calculations are made upon the atoms and their ions. In studying pyridine a SCF procedure is used and the approximations due to Pariser and Parr [*7*] are introduced. The method resembles one due to Pople [*8*]. Since one of the approximations introduced is neglect of the overlap matrix between non-orthogonal basis set functions, we investigate the effect of this assumption upon the atomic calculations in order to

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obtain some indication of the effect of the assumption alone upon an investigation of the basis of KOOPMANS' theorem and related matters.

The SCF Equations

The operator proposed by BIRSS and FRAGA [*1*] is:

$$
\begin{aligned}
R^{\mu\alpha} &= \Sigma_k\, r_k^{\mu\alpha};\\
r_k^{\mu\alpha} &= |\,\varphi_k^{\mu\alpha}\rangle\langle\varphi_k^{\mu\alpha}\,|\,F_k^{\mu\alpha}) - \Sigma_l\,|\,\varphi_k^{\mu\alpha}\rangle\langle\varphi_k^{\mu\alpha}\,|\,F_l^{\mu\alpha}\,|\,\varphi_l^{\mu\alpha}\rangle\langle\varphi_l^{\mu\alpha}\,| + \\
&\quad + |\,\varphi_k^{\mu\alpha}\rangle\langle\varphi_k^{\mu\alpha}\,|\,F_k^{\mu\alpha}\,|\,\varphi_k^{\mu\alpha}\rangle\langle\varphi_k^{\mu\alpha}\,| - \Sigma_l\,|\,\varphi_l^{\mu\alpha}\rangle\langle\varphi_l^{\mu\alpha}\,|\,F_l^{\mu\alpha}\,|\,\varphi_k^{\mu\alpha}\rangle\langle\varphi_k^{\mu a}\,| + \\
&\quad + (F_k^{\mu\alpha}\,|\,\varphi_k^{\mu\alpha}\rangle\langle\varphi_k^{\mu\alpha}\,|
\end{aligned}
$$

where the superscripts $\mu\alpha$ indicate that the k, l summations are to be taken over occupied orbitals bearing the symmetry designation μ (species) and α (subspecies). The Hartree-Fock operators are defined by:

$$F_k^{\mu\alpha} = f_k^\mu [H + \Sigma_l\, f_l^\mu\, I_l^{\mu\nu} + \Sigma_{m\ \nu,\ \beta \neq \alpha}\, f_m^\nu\, I_m^{\nu\beta}]$$

in which f_k^μ is the fractional occupancy of the k shell of symmetry designation μ, H is the one-electron operator containing the kinetic and nuclear potential terms and the operators $I_l^{\mu\alpha}$, $I_m^{\nu\beta}$ are defined by:

$$I_m^{\nu\beta} = 2\, a_{km}^{\mu\alpha,\,\nu\beta}\, J_m^{\nu\beta} - b_{km}^{\mu\alpha,\,\nu\beta}\, K_m^{\nu\beta} \ .$$

The J and K operators are the coulomb and exchange operators; the a and b are parameters related to the particular state of the configuration under consideration.

The operator $R^{\mu\alpha}$ has as eigenfunctions all occupied orbitals bearing symmetry designation $\mu\alpha$, regardless of their occurrence in open- or closed-shells:

$$R^{\mu\alpha}\,\varphi_k^{\mu\alpha} = \theta_{kk}^{\mu\alpha}\,\varphi_k^{\mu\alpha} \ .$$

The eigenvalue $\theta_{kk}^{\mu\alpha}$ is related to the orbital energy, $\eta_k^{\mu\alpha}$ by:

$$\eta_k^{\mu\alpha} = \theta_{kk}^{\mu\alpha}/f_k^\mu \ .$$

The LCAO form of the eigenvalue equation is the matrix equation:

$$\boldsymbol{R}^{\mu\alpha}\,\boldsymbol{C}_k^\mu = \theta_{kk}^{\mu\alpha}\,\boldsymbol{S}^{\mu\alpha}\,\boldsymbol{C}_k^\mu \ .$$

The column vector $\boldsymbol{C}_k^\mu$ contains the linear expansion coefficients arising from the LCAO expansion of orbital $\varphi_k^{\mu\alpha}$:

$$\varphi_k^{\mu\alpha} = \Sigma_p\,\chi_p^{\mu\alpha}\,C_{pk}^\mu = \chi^{\mu\alpha}\,\boldsymbol{C}_k^\mu$$

where $\chi^{\mu\alpha}$ is a row vector whose components are the basis set functions $\chi_p^{\mu\alpha}$. The matrix $\boldsymbol{R}^{\mu\alpha}$ has the elements:

$$R_{pq}^{\mu\alpha} = \langle\chi_p^{\mu\alpha}\,|\,R^{\mu\alpha}\,|\,\chi_q^{\mu\alpha}\rangle \ .$$

Similarily:

$$S_{pq}^{\mu\alpha} = \langle\chi_p^{\mu\alpha}\,|\,\chi_q^{\mu\alpha}\rangle \ .$$

Further expansion of the matrix $\boldsymbol{R}^{\mu\alpha}$ in terms of matrices involving the vector $\boldsymbol{C}_k^\mu$ and the elements:

$$F_{k,\,pq}^{\mu\alpha} = \langle\chi_p^{\mu\alpha}\,|\,F_k^{\mu\alpha}\,|\,\chi_q^{\mu\alpha}\rangle$$

may be found in reference [*3*].

Accurate Atomic Calculations

Calculations were performed upon the systems He, He^+, Li, Li^+, Be, Be^+ using as basis set functions the 1*s*, 2*s* and 3*s* Slater orbitals. The orbital exponents chosen are given in Tab. 1, identical exponents being used for the ion and its parent system. A programme was prepared for the IBM 1620 computer which calculated the constituent integrals and matrices and carried out the SCF calculation. The criterion for self-consistency was agreement of two successive sets of linear coefficients to five decimal places. The results of the calculations are displayed in Tab. 2, along with derived quantities and the experimental ionization energy. The SCF coefficients are given in Tab. 1.

Table 1

Orbital exponents, ζ and linear coefficients (C_k) for occupied orbitals in accurate atomic-calculations

System		Slater Orbital		
		1*s*	2*s*	3*s*
He^+	C_{1s}	1.00	0.00	0.00
He	C_{1s}	0.95	0.16	0.01
	ζ_{He}	2.000	0.575	0.100
Li^+	C_{1s}	1.00	−0.02	−0.01
Li	C_{1s}	1.01	−0.04	−0.01
	C_{2s}	−0.12	1.02	0.00
	ζ_{Li}	2.700	0.650	0.300
Be^+	C_{1s}	1.00	−0.02	0.00
	C_{2s}	−0.18	1.03	−0.04
Be	C_{1s}	1.00	−0.01	0.00
	C_{2s}	−0.20	1.02	−0.02
	ζ_{Be}	3.700	0.975	0.300

These results can be examined from two points of view: with regard to the accuracy of prediction of experimental ionization potentials by the calculated value; second, as an indication of the validity of the application of Koopmans' theorem.

The percentage errors in the calculated ionization potentials compared to experimental are: He 13%; Li 2%; Be 10%, the experimental value always being larger. This is the degree of accuracy one has come to expect in such calculations due mainly to the neglect of the correlation energy and, perhaps, in the present calculation, the non-optimum values of the orbital exponents. The relative discrepancies are what one would expect from a consideration of correlation effects. The main contribution to correlation energy is from electron pairs in the same orbital [*11*]. No orbital pair correlations are greatly disturbed in the ionization of lithium whereas in helium and beryllium the 1*s* and 2*s* electron pair correlations are removed upon ionization. The inclusion of correlation energy would lower the state energies of the lithium atom and ion by approximately equal amounts; the atom state energies of the other systems would be lowered considerably more than the corresponding ion energies.

In considering the validity of the application of Koopmans' theorem as a means of calculating ionization potentials, one can investigate the basic assumption of identical corresponding orbitals in the ion and its parent system. Examination of the linear coefficients in Tab. 1 does not reveal any startling differences although the identity of corresponding orbitals is more closely approached in progressing along the sequence, helium, lithium, beryllium.

As a further criterion we have shown in Tab. 2 the difference between the ionization potential, determined from the calculated energies of ion and parent, and the highest occupied orbital energy. In the last column of the table the percent contribution of the highest orbital energy to the total calculated energy is displayed. There is a strong correlation between these quantities. Hence it appears that the approximation will become more accurate the larger the system and, in fact, even with a system as small as beryllium the approximation is already quite good.

Table 2

Total electronic energy (E), calculated ionization potential (I_c), highest orbital energy (E_v), experimental energy and related quantities for accurate atomic calculations. Hartree units are used

System	E	I_c	E_v	Expt.	$E_v + I_c$	$\% \frac{E_v}{E}$
He$^+$	−2.000					
He	−2.787	−0.787	−0.824	0.903	−0.037	33
Li$^+$	−7.224					
Li	−7.418	0.194	−0.198	0.198	−0.004	3
Be$^+$	−14.247					
Be	−14.556	0.309	−0.312	0.342	−0.003	2

It is interesting to note that, even though the basis of KOOPMANS' theorem is not strictly valid, *i. e.*, corresponding orbitals in related systems are not identical, the highest orbital energy is nevertheless a better approximation to the true ionization potential than the calculated ionization potential.

The Approximation of Neglect of Overlap

In many applications of the LCAO MO technique the overlap between members of a non-orthogonal basis set is neglected. Although some justification of this assumption can be given [*2*], it can be shown that a true Hartree-Fock SCF calculation is not being performed when it is used.

The correct matrix eigenvalue equations for a set of non-orthogonal basis functions is:

$$\boldsymbol{R}^{\mu\alpha} \boldsymbol{C}^{\mu}_{k} = \theta^{\mu\alpha}_{kk} \boldsymbol{S}^{\mu\alpha} \boldsymbol{C}^{\mu}_{k} \ ,$$

or, for a closed-shell system in the equivalent form given by ROOTHAAN [*9*]:

$$\boldsymbol{F} \boldsymbol{C}_k = \varepsilon_k \boldsymbol{S} \boldsymbol{C}_k \ .$$

If the basis functions are now taken to be orthogonal and the same one- and two-electron integrals are retained in the formation of the matrix $\boldsymbol{F}$ (or, $\boldsymbol{R}^{\mu\alpha}$), one has:

$$\boldsymbol{F} \boldsymbol{C}_k = \varepsilon_k \boldsymbol{C}_k \ .$$

These equations would be equivalent if:

$$\boldsymbol{M}^{\dagger} \boldsymbol{F} \boldsymbol{M} = \boldsymbol{F}$$

where $\boldsymbol{M}$ is the matrix such that:

$$\boldsymbol{M}^\dagger \boldsymbol{S} \boldsymbol{M} = \boldsymbol{I} \ ,$$

the unit matrix.

Roothaan [9] has shown that $\boldsymbol{F}$ is invariant only under an unitary transformation; but, since one can rewrite the latter equation as:

$$\boldsymbol{S} = (\boldsymbol{M} \boldsymbol{M}^\dagger)^{-1}$$

which becomes, if $\boldsymbol{M}$ is unitary:

$$\boldsymbol{S} = \boldsymbol{I}^{-1} = \boldsymbol{I} \ ,$$

the requirement that $\boldsymbol{M}$ shall be unitary implies that $\boldsymbol{S}$ must be the unit matrix. Thus the matrix $\boldsymbol{F}$ is invariant under the given unitary transformation only if the basis functions upon which it is based are orthogonal. Thus the matrix $\boldsymbol{F}$ defined in terms of non-orthogonal basis functions whose corresponding overlap matrix is assumed to be the unit matrix is not a proper representation of the Hartree-Fock operator.

Atomic Calculations with Neglect of Overlap

In these calculations the basis set was the same as that used in the accurate calculations. The linear coefficients are given in Tab. 3, the total energies and related quantities are given in Tab. 4.

Table 3

Linear coefficients (C_k) for occupied orbitals in the atomic calculations with neglect of overlap

System		Slater Orbital		
		1s	2s	3s
He$^+$	C_{1s}	0.96	0.27	0.00
He	C_{1s}	0.93	0.37	0.00
Li$^+$	C_{1s}	0.98	0.21	0.02
Li	C_{1s}	0.97	0.25	0.04
	C_{2s}	−0.24	0.83	0.50
Be$^+$	C_{1s}	0.98	0.18	0.00
	C_{2s}	−0.18	0.95	0.24
Be	C_{1s}	0.98	0.20	0.00
	C_{2s}	−0.19	0.94	0.28

Table 4

Total electronic energy (E), calculated ionization potential (I_c), highest orbital energy (E_v) for the atomic calculations with neglect of overlap. Hartree units are used

System	E	I_c	E_v	Expt.	$E_v + I_c$
He$^+$	−2.125				
He	−2.980	0.855	−0.877	0.903	−0.022
Li$^+$	−7.437				
Li	−7.622	0.185	−0.198	0.198	−0.013
Be$^+$	−14.725				
Be	−15.000	0.275	−0.271	0.342	0.004

Comparison of the coefficients with those in Tab. 1 shows that the approach to identity of the corresponding orbitals of ion and parent are very similar in the two sets of calculations; further, the various quantities given in Tab. 4 exhibit the same trends as those for the accurate atomic calculations. It may be concluded that, although the total energies are no longer reliable, comparisons between the ion and parent states, which is the basis of the test of KOOPMANS' theorem, are still reliable.

Calculations on the π System of Pyridine

The π molecular orbitals were expanded in terms of symmetry functions constructed as linear combinations of atomic $2px$ orbitals. (It should be noted that this is a necessary step in the formalism of the R operator since the symmetry characteristics of the molecular orbitals are used to ensure orthogonality between orbitals of different symmetry designation.) Numbering the centres consecutively from the nitrogen atom as centre 1, the basis functions are:

$$\begin{aligned}
\chi_1^{B_1} &= \frac{1}{\sqrt{2}}(2\,px_2 + 2\,px_6) \;; & \chi_3^{B_1} &= 2\,px_4 \;; \\
\chi_2^{B_1} &= \frac{1}{\sqrt{2}}(2\,px_3 + 2\,px_5) \;; & \chi_4^{B_1} &= 2\,px_1 \;; \\
\chi_1^{A_2} &= \frac{1}{\sqrt{2}}(2\,px_2 - 2\,px_6) \;; & \chi_2^{A_2} &= \frac{1}{\sqrt{2}}(2\,px_3 - 2\,px_5) \;.
\end{aligned}$$

The superscripts B_1, A_2 indicate the irreducible representation of the group C_{2v} to which the function serves as a basis.

The integrals over these basis functions were calculated in terms of the atomic integrals tabulated in Tab. 5 and 6. These were calculated from data given in the literature [6]. That these may or may not be the best values is not in question; it is sufficient for our purpose that they be typical of those used in PARISER-PARR type calculations.

Table 5

Core integrals for the pyridine calculation. The upper triangle of a symmetric matrix is displayed, with entries:

$$C_{ij} = -\langle 2px_i \mid H_{\text{core}} \mid 2px_j \rangle$$

Electron volts are used

46.04	2.58	–	–	–	2.58
	42.02	2.40	–	–	–
		41.78	2.40	–	–
			41.71	2.40	–
				41.78	2.40
					42.02

Table 6

Two-electron integrals for the pyridine calculation. The upper triangle of a symmetric matrix is displayed with entry $J_{ii,jj}$, in the (i, j) position: Electron volts are used

12.30	7.68	5.60	4.97	5.60	7.68
	10.50	7.30	5.46	4.90	5.46
		10.50	7.30	5.46	4.90
			10.50	7.30	5.46
				10.50	7.30
					10.50

The results of the SCF calculations upon pyridine and its positive ion are given in Tab. 7. The difference in energy between the ion and parent was 0.424 Hartrees, identical to the negative of the highest occupied orbital energy. This agreement is reflected in the near-identity of the corresponding orbitals of the two systems. It is further confirmation of the hypothesis that the basis of Koopmans' theorem is valid when the contribution of the orbital energy for the ionized electron is a small fraction of the total electronic energy of the parent system.

Table 7

Linear Coefficients (C_k^μ) for the pyridine molecule and ion molecular orbitals

System		Basis Function			
		χ_1	χ_2	χ_4	χ_4
C_5H_5N	$C_1^{B_1}$	0.57	0.52	0.32	0.53
	$C_2^{B_1}$	−0.27	0.49	0.58	−0.59
	$C_1^{A_2}$	0.69	0.73	–	–
$C_5H_5N^+$	$C_1^{B_1}$	0.57	0.49	0.35	0.57
	$C_2^{B_1}$	−0.25	0.51	0.60	−0.56
	$C_1^{A_2}$	0.69	0.72	–	–

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