Comment on the Luken-Sinanoğlu paper "Theory of atomic structures including electron correlation. V. Excited states not lowest of their symmetry and oscillator strengths in neutral and singly ionized atoms"

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(Received 15 April 1976; revised manuscript received 6 October 1977)

A recent paper by Luken and Sinanoğlu (Phys. Rev. A 13 1293, 1976) has criticized some of our work and contains material on excited states and oscillator strengths. We suggest that satisfaction of upper boundedness via the Hylleraas-Undheim-MacDonald theorem is neither a sufficient nor a necessary condition for obtaining reasonably accurate oscillator strengths. Our method for truncated Hamiltonian matrices which chooses the root which minimizes the energy as well as the correlation overlap $\langle X/X \rangle$ in fact yielded upper bounds and did not suffer a "variational collapse." We point out that for excited valence states embedded in Rydberg or continuum series, the f values are *very* sensitive to (a) choice of basis sets and (b) *Relative* position of diagonal matrix elements. The N I $^4S^o \rightarrow 2s2p^4\ ^4P$, B I $^2P^o \rightarrow 2s2p^2\ ^2S$, C I $2p^2\ ^3P \rightarrow 2s2p^3\ ^3P^o$ transitions serve as examples.

I. INTRODUCTION

In a recent paper,[1(a)] Luken and Sinanoğlu discussed and criticized our previous work[2,3] on calculations of excited states and oscillator strengths. The purpose of this article is to offer our opinion on this subject. Certain aspects of the theory of excited states are reviewed and new results are presented which may be helpful to current research on excited-state wave functions and photoabsorption cross sections.

Embedded in or apart from the criticism, there are two main themes in the Luken-Sinanoğlu papers.

(a) A discussion of states having lower states of the same symmetry and the application of the Hylleraas-Undheim-MacDonald (HUM) theorem to obtain wave functions which avoid "variational collapse" and are therefore suitable for the calculation of oscillator strengths. For example, in Ref. 1(b), p. 1495, third paragraph, they write: 'In the calculations of Nicolaides such "variational collapse" has occurred as first noted in print by Hibbert, and confirmed in another paper in which the problem is analyzed and *proper application of variational theory making use of the Hylleraas-Undheim-MacDonald (HUM) theorem* is indicated. The f values of Nicolaides have shown serious discrepancies with experimental values and *this is due to variational collapse*. In the present work we calculate the variationally correct NCMET charge wave functions for states not lowest of their symmetry for the first time.'

(b) NCMET as "the new atomic structure theory" applied to the calculation of accurate oscillator strengths. For example, in Ref. (a), p. 1293, they write: "Sinanoğlu showed in the non-closed shell generalization of his MET, which we refer to as NCMET, that electronic charge distributions, $\rho(r)$, and the resulting "charge-like properties," like electronic quadrupole moments, hyperfine constants, form factors, also transition densities $\rho_{on}(r)$ and the resulting oscillator strengths, etc. should be given to high accuracy just from what he called the "charge distribution wave function Ψ_{CD}," or the "charge wave function Ψ_C" for short."

The present paper suggests, with detailed arguments and concrete numerical examples, that (i) the Luken-Sinanoğlu discussion and sweeping statements on these topics and the emphasis on certain points pertaining to variational theory, the calculation of wave functions, energies and transition probabilities are, to a large extent, debatable. (ii) Their "new" computational procedures for the accurate calculation of oscillator strengths contain worrisome approximations. (iii) The calculated electronic structure of valence states and perturbed continuum and discrete series is very sensitive to the details of quantum-mechanical computations, regardless of whether the HUM theorem is satisfied or not.

II. THE 1972 NICOLAIDES-BECK WORK ON VALENCE EXCITED STATES

Our calculations of Ref. 2 have not suffered from a "variational collapse," as it is claimed in Ref. 1. The reasons for the discrepancy between theoretical and experimental f values presented in Ref. 3 is due mainly to inefficiency of basis functions and is briefly analyzed below. We recall the following definition: Let E_n be the exact energy (i.e., an eigenvalue of Schrödinger's equation) of the nth quantum state of a given system, with

$E_n > E_{n-1} > \cdots > E_1$. Consider a trial function $\tilde{\psi}_n$ such that

$$\tilde{E}_n = \frac{\langle \tilde{\psi}_n | H | \tilde{\psi}_n \rangle}{\langle \tilde{\psi}_n | \tilde{\psi}_n \rangle} > E_n . \quad (1)$$

Then we say that $\tilde{E}_n$ is an upper bound of the exact energy E_n and no variational collapse has occurred. Our calculations[2] satisfied $\tilde{E}_n > E_n$ in all cases.

Also, if one insists (incorrectly[4]) that there is such a thing as a "partial variational collapse" for truncated Hamiltonian matrices, then, a look at Table III of Ref. 1(a), which states that our results are not "variational bounds on the energies of the states indicated here," shows that out of the *six* examples chosen to be shown by Luken and Sinanoğlu, in *three* cases their energies have gone *below* ours and therefore their calculations should also suffer from "partial variational collapse"!

In our early work on excited states,[2,3] the types of correlation and basis functions were chosen according to the NCMET classification scheme. The problem of lower states, within the NCMET scheme, was pointed out for the first time and we discussed how it could be treated according to the separation theorem of eigenvalues [Ref. 2, Sec. 3. Also compare Eq. 11 of Ref. 2 with the discussion of L-S Ref. 1(a), p. 1302 on the B I ^2S state.] On the other hand, it was also pointed out that, due to the smallness of the set of basis functions employed (in the spirit of NCMET[11,14]), the matrix representation of the Hamiltonian within this set did not correspond to the real spectrum and an alternative approach was taken: the desired solution was chosen as the vector with the largest coefficient in the H-F function representing the configuration of interest (i.e., *for which energy as well as correlation is minimized*). We remarked how the choice of the basis functions may result in multiple minima and root crossings and affect the mixing coefficients. In fact our calculations indicated that the flexibility of one optimized STO in describing complete sets of H-F orbitals is limited in cases where there is strong valence-Rydberg mixing. [We point out that similar situations may occur in multiconfigurational Hartree-Fock (MCHF) calculations in excited states (e.g., Ref. 5). A related discussion has been given recently by Grein and Banerjee (Ref. 6, see their Sec. 3).]

In the calculations of the oscillator strengths[2,3] we did not use the "charge-distribution" arguments [Ref. 1(a), p. 1293], which we feel are unsubstantiated. Instead, we wrote $\langle \Psi^I_{\text{exact}} | \vec{D} | \Psi^F_{\text{exact}} \rangle \approx \langle \Psi^I_{\text{CD}} | \vec{D} | \Psi^F_{\text{CD}} \rangle$ (Eq. 1 of Ref. 3 and Eq. 13 of Ref. 2) and worked within this scheme. We found out that for states in neutrals and some singly ionized atoms, regardless of whether they had lower states of the same symmetry or not, the types of correlation effects and the basis sets were clearly not flexible enough to account for details of configuration interaction and their effect on oscillator strengths (see Ref. 3 abstract and *p*. 243). Our emphasis on the above equation, i.e., *on the characteristics of the amplitude rather than on the characteristics of the wave function*, eventually resulted in a first-order theory of oscillator strengths,[7-10] FOTOS, which uses flexible basis sets and appears to be a valid theory of photoabsorption.[9]

III. THE ÖKSUZ-WESTHAUS-LUKEN-SINANOĞLU NCMET CALCULATIONS

The early Westhaus-Nicolaides-Sinanoğlu calculations of oscillator strengths[11-13] were carried out using NCMET[15] wave functions obtained by Öksüz and Sinanoğlu[14] for studies of energetics. The use of such wave functions was based on practical reasons, i.e., availability. This is why no results for other types of transitions (e.g., shell jumps) were reported. Thus, these calculations might be considered as not a result of any theory of oscillator strengths.

The relative success of the Westhaus NCMET calculations was really observed only in *ions* of first row atoms. The only calculation on a neutral, N I $^4S^0 - {}^4P$, was not accurate.

The reason for such discrepancies is to be found in the characteristics of the wave functions employed and their ability to describe the transition amplitude correctly. By now, it is established that in ionized species, this can be done routinely using limited configuration-interaction or low-order perturbation theory. However, for states in neutrals and for a few singly or even doubly ionized species, whether they are the lowest of their symmetry or not, there is strong mixing of certain configurations and the choice of the basis sets is very crucial and still not understood completely.

The new NCMET calculations of Ref. 1 have employed wave functions of the excited state with a slightly expanded basis set (i.e., they have added one orbital of l symmetry, where l is the symmetry of the Rydberg orbitals belonging to the series which interacts with the valence configuration). Thus, what Luken and Sinanoğlu have essentially done in the four papers of Ref. 1, is to use the same ground-state wave functions[2] while to the excited-state functions of Ref. 2 they added a vector corresponding to the Rydberg configuration (thus changing the basis set), and

diagonalized.

However, there is no guarantee that their choice of the basis functions is the correct one. Neutral and singly ionized systems may often exhibit substantial nonorthonormality effects (between initial and final states) irrespective of whether the states involved are of the lowest energy for their symmetry or not, which requires[7] the presence of certain *bivirtual* configurations, none of which are present in the L-S work.

Furthermore, they partially neglect the effect of nonorthonormality among Hartree-Fock orbitals corresponding to valence and Rydberg configurations used in the Hamiltonian matrix (e.g., the SCF-HF $2p$ from O I $1s^22s2p^5\,{}^3P^0$ and the SCF-HF $\widetilde{2p}$ from O I $1s^22s^22p^33s\,{}^3P^0$ do not satisfy $\langle 2p/\widetilde{2p}\rangle = 1$). They use an orthonormal basis set constructed from the lowest Rydberg member which is not of primary interest to them (see Ref. 1(a), p. 1301). This arbitrary choice should be particularly worrisome because it is highly unlikely that the inherent error is corrected sufficiently by the use of a single polarization function of each symmetry, taken one at a time (e.g., they neglect pair excitations which are needed simply because a common orthonormal set is used). In this regard, one may suspect both their energy results (L-S Table III), which will have $|\Delta E|$ increased by the missing effects, and the oscillator strengths.

Finally, for states very sensitive to positioning, as are the O I ${}^3P^0$ states, the failure to include certain pair bivirtual correlations (beyond those required for nonorthonormality reasons) which would affect the relative positions of the valence and Rydberg vectors differently, gives rise to further uncertainties.

We close by commenting on the footnote c of Table II of LS.

The claim that the restriction $\zeta_{3s} = \zeta_{3p} = \zeta_{3d} = \frac{5}{3}\zeta_{4f}$, is sufficient to prevent variational collapse, is incomprehensible to us. Given a system in which there is heavy Rydberg-valence configuration interaction, the sequence of the eigenvalues of the diagonalized matrix often depends exclusively on the characteristics of the virtual orbitals describing the Rydberg series orbitals. Thus a particular choice of that orbital may result in one sequence and another one in an inverted one (i.e., there is root crossing as a function of the parameters of the virtual orbital). The requirements that one places on the virtual orbitals of other symmetries is immaterial.

This choice by Oksüz and Sinanoğlu,[14] which was applied to calculations of ground as well as excited states with lower-lying states (e.g., N II $2s2p^3\,{}^1P^0$, N I $2s2p^4\,{}^4P$, O II $2s2p^4\,{}^2P$ and O I $2s2p^5$-${}^3P^0$—Table 5 of Ref. 14) seems to have been just a calculational recipe for computations which always chose the lowest root of the diagonalized matrix as the desired solution regardless of the actual position of these states in the real spectrum. This is confirmed by a related statement on p. 48 of Ref. 14 and the footnote of Table 5, Ref. 14.

IV. A COMMENT OF THE HYLLERAAS-UNDHEIM-MacDONALD THEOREM AND OSCILLATOR STRENGTHS

The HUM theorem provides *upper bounds* to the corresponding exact energies. It says nothing about how close the approximate solutions are to the real ones. It simply says that if one keeps on adding terms, there is uniform convergence for states lying below. Furthermore, the root ordering depends on the choice of the basis functions.

Even if the root ordering is correct, the corresponding wave functions may be so inaccurate as to be worthless. For example, from an $M \times M$ matrix HF calculation of unperturbed Rydberg states of the N-electron system, one may obtain bounds to the first M states. But, such additional solutions are characteristic of the $N+1$ electron system and are thus unlikely to yield "good" (i.e., SCF-HF) f values. The same goes for many-electron, correlated functions. Upper bounds may be obtained but the accuracy of the resulting f values is another matter. Hence, the HUM theorem is by no means a sufficient condition for accurate f values. Is it a necessary one? We think not. For example, a direct numerical HF solution of a high-lying Rydberg state, in which no lower states are explicitly represented, may yield reasonable results (e.g., energy differences between Rydberg members, f values, etc.). Furthermore, in cases of calculations of highly excited state wave functions,[20] one may be able to remove configurations of lower energy which are far from the interaction region, providing they do not possess a large f value.

The carbon example discussed in Sec. V B offers further support to the conclusion that HUM may not be necessary.

V. EXAMPLES FROM MANY-BODY CALCULATIONS

A. The N I $1s^2\,2s2p^4\;{}^4P$ state

This state offers a good opportunity to substantiate arguments made in this paper. It is very close to the N I $1s^22s^22p^2ns$ and nd series and its lifetime has been measured accurately.[16,17]

We have performed a series of relatively large configuration-interaction calculations on this

TABLE I. Effect of basis set on N I $2p^3\,{}^4S^o \rightarrow 2s\,2p^4\,{}^4P$ f value (length form).

Calculation type	H-F coefficient	f_L
A^a	0.910	0.084
B^b	0.716	0.002
C^c	0.975	0.145
D^d	0.754	0.035
Experiment		0.0.82,[e] 0.85[f]

[a]A FOTOS calculation (Ref. 7) using 3s and 3d H-F functions. "$2s2p^4$" was the second root.

[b]Same basis as A except the 3s was replaced by an STO from earlier (Ref. 2) work. Again "$2s2p^4$" was the second root. Little variation in energies between A and B was found.

[c]References 11 and 14. The "$2s\,2p^4$" was the lowest root, contrary to the experimental ordering.

[d]From L-S, Table II.

[e]Barry *et al.*, Ref. 16.

[f]Kernahan *et al.*, Ref. 17.

state. In calculation A, the 3s, and 3d functions were H-F functions calculated numerically using Froese-Fisher's code. The ordering of the roots were as observed experimentally, i.e., the lowest had the largest coefficient in front of the $1s^22s^22p^23s\,{}^4P$ H-F vector, the second lowest in front of the $1s^22s2p^4\,{}^4P$ H-F vector.

The mixing coefficients were such that we obtained oscillator strengths in good agreement with experiment (see Table I).

In calculation B we changed *only* the 3s function and instead of a HF 3s we used an STO. Everything else remained the same. The energy position hardly changed. The root ordering remained the same. However, the coefficient of the H-F vector of the *second root* was different and consequently the f- value was changed drastically. This calculation has not suffered a variational collapse. Simply, the basis set is such that it yields the wrong mixing coefficients.

Calculation C is the Westhaus-Öksüz-Sinanoğlu[11,14] calculation. No multidimensional optimization was carried out. The $2s2p^4\,{}^4P$ root was the *lowest*, contrary to the experimental spectrum. However, the H-F coefficient resembled the true one more than that of calculation B. Thus, agreement of the f- value with experiment is better even though the root ordering is wrong.

Calculation D is as described in L-S.

B. The C I $2s2p^3\,{}^3P^o$ state

In order to reinforce the point made in Sec. V A, we note that our old, without HUM, C I ${}^3P$ - ${}^3P^0$ f-value[3] (f = 0.092), is in excellent agreement with Weiss's very large C I calculation[18] (f = 0.097), which disagrees with that of L-S (f = 0.038), although both satisfied HUM'S theorem. A recent phase-shift experiment[19] has yielded f = 0.063.

C. The B I "$2s2p^2$" ${}^2S$ state

This state is embedded between the n = 6 and n = 7 members of the $1s^22s^2ns\,{}^2S$ Rydberg series.[10] Our "HUM-less" calculations[2,3] yielded an f_L value of f 0.083. Nesbet's recent calculations,[21] which included a large number of Rydberg orbitals, yielded f_L = 0.0004. FOTOS[10] yields f_L = 0.024. The experimental value[22] is f = 0.035. This example demonstrates once again how sensitive such f values are to basis sets and the relative positions of the diagonal matrix elements.

In our computations of transition probabilities to energy regions of valence-Rydberg configuration mixing,[8,10,20] the excited states of interest are represented in zeroth order by SCF-HF functions. As for the relative positions of the diagonal matrix elements, these are obtained by a straightforward effective Hamiltonian approach[9,10] which essentially accounts for the difference in the types of correlation present in the valence and Rydberg states.

VI. CONCLUSION

The energies computed in Ref. 2 are *upper bounds* to the exact energies.

The variational-collapse arguments put forth by Luken and Sinanoğlu are irrelevant. Rather, in most excited-state calculations of the variational configuration-interaction type with H-F zeroth-order functions, it is the flexibility of the basis functions which is the determining factor, in the following sense.

(a) If the flexibility is such that it allows a one-to-one correspondence between roots of the diagonalized matrix and the physical spectrum, then the HUM applies directly and the desired solution for the nth state is obtained by choosing the nth root. *For the nth root,* $\langle X|X\rangle$ = min *(where X is the correlation function) if the zeroth-order choice is* H-F. *It does not however necessarily mean that the wave function corresponding to this root is a good representation of the exact wave function, expecially in cases of near- degeneracies of the diagonal matrix elements.*

(b) If the basis set is such that it does not allow the direct application of the separation theorem, then the choice of the desired vector according to the prescription: Energy = min, $\langle X|X\rangle$ = min, was suggested as a reasonable alternative.[23-25]

Due to the physical basis of the independent-particle approximation no variational collapse occurs. If the flexibility of the STO's describing

Rydberg (continuum) series into which a valence configuration is embedded and the corresponding diagonal energies happen to be good (we currently always include H-F functions surrounding the valence state while in cases of serious near-degeneracies, the diagonal matrix elements are adjusted semiempirically by the down-shift model[10]) then the mixing coefficients of the most important vectors are reasonably accurate and good oscillator strengths can be obtained.

To clarify the point further in order to avoid possible misunderstandings: satisfaction of the HUM theorem by inclusion of the necessary configurations, presupposes an analogous flexibility of basis sets. For example, take the N I $1s^22s2p^4\,{}^4P$ state. For the semi-internal correlation we have the vectors $1s^22s^22p^2f_s$ and $1s^22s^22p^2f_d$. Now, if we approximate $f_s \approx 3s$ STO, $f_d \approx 3d$ STO (see Ref. 14, p. 48) then the CI matrix contains only *three* configurations: $1s^22s2p^4$, $1s^22s^22p^2$"$3s$", $1s^22s^22p^2$"$3d$". If the semi-internal orbitals are made *more flexible* and instead of one STO we expand them in terms of *three* STO's, then: e.g., $f_s = 3s + 4s + 5s$, $f_d = 3d + 4d + 5d$, and we have a 7×7 CI, i.e., flexibility of orbital basis sets and number of configurations *is* the same thing.

However, satisfaction of HUM's theorem has nothing to do with the accuracy of oscillator-strength calculations directly. Only indirectly it may have, since one is forced to increase the flexibility of the basis set describing Rydberg, continuum series. Yet, it is not at all clear that, given a highly excited valence state, "far away" Rydberg states need to be included, even though they may be lower.

Our old calculations,[2,26] which were carried out within the NCMET classification scheme, may, in some cases, suffer from lack of flexibility of the basis functions in spite of the multi dimensional optimization procedures.[2] These problems may exist for levels lowest of their symmetry[26] as well as for levels which are not the lowest.

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[4]We say "incorrectly" because the concept of variational collapse is known to be an energetic one. The approximate energy is either above or below the exact one. In practice, it is not easy to establish a definition and criteria for the notion "wave-function variational collapse." The approximate wave function of a given state is either accurate or not with respect to an observable. The dependence of the mixing coefficients on the characteristics of the truncated Hamiltonian matrices and the basis sets, is discussed in the text. If a CI expansion is made, the signs of the various configurations which enter the expansion depend on the manner by which they were made eigenfunctions of the symmetry operators and on the phases of the one-particle radial functions at the origin.

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[23]We note that this approach, i.e., minimization of the correlation vector overlap, is similar in spirit to the stabilization method for resonances [H. S. Taylor, Adv. Chem. Phys. 18, 91 (1970)] which also bypasses the necessity to include all the lower states of the same symmetry. However, in the continuum there is no rigorous minimum principle for the autoionizing state, although simple variational constraints (see Refs. 20, 24, and 25) seem to work energywise. A serious problem with autoionizing-states calculations where the continuous spectrum is approximated by square-integrable correlation vectors (Ref. 24) is that the position of the pseudocontinuum vectors is rather arbitrary and therefore the determination of the correct mixing coefficients is difficult to ascertain.

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[26]For example, see O. Sinanoğlu, Nucl. Instrum. Methods 110, 193 (1973), Tables 1, 2, and 6, where a number of f values are presented under the title "NCMET—this work." The Be I $2s2p\,^1P^o$-$2p^2\,^1D$ and Cl III $3s^23p\,^3\,^4S^o$-$3s3p^4\,^4P$ NCMET f values (0.020 and 0.085, respectively, for the length form, 0.016 and 0.103 for the velocity form) differ considerably from the accurate ones [A. Hibbert, J. Phys. B 7, 1417 (1974), $f_{\mathrm{Be}}=0.0007$; S. Bashkin and I. Martinson, J. Opt. Soc. Am. 61, 1686 (1971), $f_{\mathrm{Cl\ III}}=0.043$] although the upper states are the lowest of their symmetry.