PHYSICAL REVIEW A VOLUME 18, NUMBER 3 SEPTEMBER 1978

Reply to "Comment on 'Theory of atomic structures including electron correlation. V.'"

William L. Luken
Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27707

Oktay Sinanoğlu
Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520

(Received 12 December 1977)

The concept of variational collapse is based on the form of a variational trial wave function and not solely on its energy. In particular, a variational calculation is said to suffer from variational collapse when a trial wave function intended to represent an excited state takes on the character of one or more states of lower energy as the energy of the trial wave function decreases. In view of this, we repeat our claims that certain calculations published by Nicolaides and Beck suffered from variational collapse, and consequently the results of these calculations do not represent the non-closed-shell many-electron theory of Sinanoğlu.

The central issue in the Comment[1] by Nicolaides and Beck on our recent work on variational calculations of excited-state wave functions[2-4] is the question of whether or not certain calculations published by Nicolaides and Beck[5,6] suffered from variational collapse. This is closely related to the question of whether or not these same calculations[5,6] represent applications of the non-closed-shell many-electron theory (NCMET) of Sinanoğlu.[7-11]

In order to indicate what is meant by "variational collapse," we must consider the expansion of an arbitrary normalized N-electron wave function Φ in terms of the complete orthonormal set $\{\Psi_i, i=1, 2, \ldots\}$ of eigenfunctions of the N-electron Hamiltonian H. That is,

$$\Phi = \sum_i C_i \Psi_i \tag{1}$$

where $H\Psi_i = E_i\Psi_i$ and $E_i \leqslant E_{i+1}$ for $i=1,2,\ldots$. The sum in Eq. (1) includes an integral over all continuum eigenfunctions of H. In addition, we shall define the energy (expectation value) functional

$$E(\Phi) \equiv \langle\Phi|H|\Phi\rangle/\langle\Phi|\Phi\rangle \tag{2}$$

and the quantities b_n, e_n, and a_n:

$$b_n \equiv \sum_i |C_i|^2 \text{ for } i \text{ such that } E_i < E_n , \tag{3a}$$

$$e_n \equiv \sum_i |C_i|^2 \text{ for } i \text{ such that } E_i = E_n , \tag{3b}$$

$$a_n \equiv \sum_i |C_i|^2 \text{ for } i \text{ such that } E_i > E_n , \tag{3c}$$

which represent the portions of Φ contributed by eigenfunctions of H with eigenvalues less than, equal to, or greater than eigenvalue E_n, respectively. Thus if Φ is an exact eigenfunction of H with eigenvalue E_n, then $E(\Phi)=E_n$, $b_n=0$, $e_n=1$, and $a_n=0$.

In the case of the lowest eigenvalue E_1, the portion b_1 vanishes because there are no states for which $E_i<E_1$. In this case, conventional (ground-state) variational theory[12] indicates that (a) $E(\Phi) \geqslant E_1$, (b) $E(\Phi)=E_1$ if and only if $e_1=1$ and $a_1=0$, and (c) as $E(\Phi)$ approaches E_1, e_1 approaches 1 and a_1 approaches 0. Therefore, if Φ is a sufficiently flexible function of a number of variational parameters, then not only is the absolute minimum of $E(\Phi)$ equal to E_1, but the corresponding form of Φ is an exact eigenfunction of H with eigenvalue E_1.

Similar methods can also be used to determine eigenfunctions of H with eigenvalues E_n greater than E_1. In such calculations, however, it is necessary to impose constraints on the trial wave functions Φ in order to prevent the occurence of "variational collapse" in which Φ progressively takes on an increasing character of one or more lower-lying eigenfunctions of H, and progressively decreasing character of the eigenfunction of interest, as its energy $E(\Phi)$ is reduced. That is, as $E(\Phi)$ decreases, b_n becomes large and increases, while e_n decreases.

Ultimately, in a case of total variational collapse, b_n will approach unity, e_n will approach zero, and $E(\Phi)$ will fall below E_n and approach E_1. In the initial stages of variational collapse, however, it is not necessary for $E(\Phi)$ to be below E_n. For many-electron atoms and molecules, it is often very difficult to get $E(\Phi)$ below E_n even when Φ is intended as an approximation to Ψ_1, especially if E_n is less than about 2 eV above E_1. Thus one may easily have a situation in which $E(\Phi)$ is greater than E_n, but b_n is large (e.g., roughly 0.1 to 0.5) and rapidly increasing as $E(\Phi)$ decreases. If such a calculation is terminated at this point, it may be said to be in a state of "partial variational collapse" in the sense that the degree of variational collapse, as measured by the value of b_n as compared to e_n, would have increased much further if the calculation had been continued.

There are several types of constraints which can be used to prevent variational collapse. The most effective of these is the use of symmetry restrictions. Thus, if Φ is restricted so as to have the symmetry of an irreducible representation of a symmetry group to which H belongs, then the coefficients C_i vanish for all eigenfunctions of H of all other symmetries. In this way, the lowest eigenfuction of H of each symmetry can be treated in the same manner as is the overall ground state.

In order to calculate variational wave functions for excited states not lowest of their symmetry additional constraints are required beyond symmetry restrictions. Suitable constraints can be achieved (a) by keeping Φ orthogonal to all of the exact eigenfunctions of H with eigenvalues less than that of the state of interest, (b) by application of the Hylleraas-Undheim-MacDonald (HUM) theorem,[13] or (c) by use of the constrained variation method.[14] Each of these methods yields variational bounds for excited-state wave functions analogous to those given by conventional variational theory for ground-state wave functions. That is, not only is $E(\Phi) \geqslant E_n$, but Φ approaches an eigenstate of H with energy E_n as $E(\Phi)$ approaches E_n.

Each of these methods, however, requires some type of explicit consideration of every eigenfunction of H with an eigenvalue less than E_n (and, if symmetry restrictions are used, having the same symmetry as the eigenfunction of interest). Such considerations can be very bothersome, especially if the number of such lower eigenfunctions is large (i.e., greater than one or two). The impact of such considerations is even more serious for autoionizing states (electron scattering resonances) for which the number of such lower states is infinite. Consequently various attempts have been made to find alternative methods for calculating wave functions of such excited states which avoid these difficulties. The "stabilization" method of Taylor,[15] for example, has been very successful in this respect.

The work of Nicolaides and Beck in question,[5,6] represents, in part, an attempt to develop yet another approach to this problem. Due to the absence of adequate constraints, however, these calculations,[5,6] as indicated previously,[2-4,16] suffered from (partial) variational collapse.

The calculations in question,[5,6] were intended to yield configuration interaction (CI) wave functions for certain electronic states assigned to $1s^2 2s^n 2p^m$ intravalency (V) configurations in neutral and singly ionized atoms. In each case, a lower-lying state of the same symmetry assigned to a $1s^2 2s^{n+1} 2p^{m-2} 3s$ Rydberg (R) configuration was also present. In addition to several other configurations, the configurational basis sets employed by Nicolaides and Beck in these calculations each included a configuration of the type $1s^2 2s^{n+1} 2p^{m-2} s(\zeta_s)$, where $s(\zeta_s)$ is a variational s symmetry virtual orbital which depends on an STO (Slater-type orbital) exponential factor ζ_s. This will be called the S configuration.

Except for the V configuration, for which a symmetry-adapted single configurational wave function was used, the basis sets used by Nicolaides and Beck were composed of L^2 and S^2 complete sets of Slater determinants. Consequently, some of the eigenvectors of the resulting CI Hamiltonian matrices correspond to symmetries which differ from the symmetry of the V state of interest. In order to simplify the following discussion, all such eigenvectors will be completely ignored, and only those eigenvectors having the same symmetry (i.e., L, S, and parity) will be considered. This is equivalent to using a basis of symmetry-adapted configurational state functions instead of Slater determinants. The only influence which the additional eigenvectors have is to alter the numbering of the eigenvectors. That is, the second eigenvector of a given symmetry, for example, may be the seventh eigenvector overall. (It is also assumed, of course, that the eigenvectors are numbered in order of increasing eigenvalues.)

The virtual orbital $s(\zeta_s)$ and the S configuration were intended to provide variational approximations to the semi-internal orbital $\hat{f}_s$ and the semi-internal configuration $1s^2 2s^{n+1} 2p^{m-2} \hat{f}_s$. Because $\hat{f}_s$ is a relatively compact orbital, localized near the $2s$ and $2p$ orbitals, this approximation corresponds to a relatively large value of ζ_s (i.e., $\zeta_s \approx 1.5$). For small values of ζ_s, however, i.e., $\zeta_s \approx 0.6$, $s(\zeta_s)$ approximates the diffuse $3s$ Rydberg orbital and the S configuration approximates the low-energy R configuration.

The calculations of Nicolaides and Beck[5,6] were initiated at a large (semi-internal-like) value of ζ_s. At this point the energy $E_S(\zeta_s)$ of the S configuration is well above the energy E_v of the V configuration, and the magnitude of the coefficient C_{v1} of the V configuration in the lowest eigenvector is larger than the magnitude of the corresponding coefficient C_{vi}, $i \geqslant 2$, in all higher eigenvectors. (Each eigenvector is normalized to unity.) Therefore, based on their interpretation of the rule "$\langle \chi | \chi \rangle$ = minimum", p. 542 of Ref. 5, Nicolaides and Beck equated the "CI energy of the V configuration," $E_v'(\zeta_s)$ to the lowest eigenvalue $E_1(\zeta_s)$ of the CI Hamiltonian matrix for this value of ζ_s.

As ζ_s decreases from this large value, the $s(\zeta_s)$ virtual orbital becomes progressively more diffuse and Rydberg-like, and $E_s(\zeta_s)$ decreases rapidly. Being independent of ζ_s, E_v remains constant. Thus as ζ_s decreases, the difference $E_s(\zeta_s) - E_v$ decreases, causing a slow decrease in $E_v'(\zeta_s) = E_1(\zeta_s)$. Nicolaides and Beck concluded that their variational approximation to the wave function of the V state was improving as ζ_s decreased. In reality, they were already in the initial stage of variational collapse, and their trial wave function was departing from the form of the desired V-state wave function, and beginning to take on the form of the lower-energy R-state wave function.

As ζ_s decreases still further, $E_s(\zeta_s)$ continues to decrease rapidly, and at some point $\zeta_s = \zeta_c$, $E_s(\zeta_s)$ crosses E_v. As ζ_s approaches this point, $E_v'(\zeta_s) = E_1(\zeta_s)$ begins to decrease very rapidly, the magnitude of C_{v_1} decreases rapidly, and the magnitude of C_{v_2}, the coefficient of the V configuration in the second lowest eigenvector increases rapidly. This continues until some point $\zeta_s = \zeta_c'$ where the magnitude of C_{v_2} exceeds that of C_{v_1}. (For a 2×2 CI, $\zeta_c = \zeta_c'$, but for an $n \times n$ CI with $n > 2$, ζ_c' is usually shifted away from ζ_c.) Therefore, based on their interpretation of "$\langle \chi | \chi \rangle$ = minimum," Nicolaides and Beck appear to switch the assignment of the V configuration from the lowest eigenvector to the second lowest eigenvector. Consequently, $E_v'(\zeta_s)$, the energy of the trail wave function for the V state, discontinuously jumps from $E_v'(\zeta_s) = E_1(\zeta_s)$ for $\zeta_s > \zeta_c'$ to $E_v'(\zeta_s) = E_2(\zeta_s)$ for $\zeta_s < \zeta_c'$, where $E_2(\zeta_s)$ is the second eigenvalue of the CI Hamiltonian matrix.

At this point, $E_v'(\zeta_s)$, which had been rapidly decreasing, abruptly increases by a large amount, i.e., $E_2(\zeta_c') - E_1(\zeta_c')$. Consequently, Nicolaides and Beck conclude that they have found a minimum in the energy of their trial wave function, and they terminate the variation of the parameter ζ_s at a value slightly greater than ζ_c'. This is the source of the "extremely sharp minimum in the energy" reported by Nicolaides and Beck on p. 546 of Ref. 5, and emphasized by them in a number of other places.

Had the variation of ζ_s been continued until a true minimum was found in either $E_1(\zeta_s)$ or $E_2(\zeta_s)$, it is possible that a good approximation to either the R- or V-state wave functions, respectively, could have been obtained. The point $\zeta_s = \zeta_c'$, however, represents nothing other than an accidental degeneracy between E_v and the energy of a nonphysical basis configuration S. This point is of no physical significance.

Furthermore, the resulting CI wave functions determined by $\zeta_s > \zeta_c'$, which Nicolaides and Beck attribute to the V state, are each in an advanced state of variational collapse, with b_2, as defined by Eq. (3a), having a value greater than 0.5 in most, if not all, cases. This is revealed by the magnitude and sign of the S configuration in each of these wave functions. For example, the *large negative* coefficient of the S configuration in their nitrogen atom ^4P wave function (see the fifth column of Table II in Ref. 2) indicates a large overlap with the corresponding R-state wave function.

Consequently, each of these "wave functions" reported by Nicolaides and Beck in Ref. 5 represents an extremely poor approximation to both the V-state wave function and the lower-energy R-state wave function. As such, it is not surprising that the f values calculated using these "wave functions" and reported in Ref. 6 differ radically from the results of other calculations,[2,3] as well as from the results of experimental measurements.

In their configuration-interaction calculations,[5] Nicolaides and Beck used sets of configurations found in the NCMET "charge wave function" of each state.[2,11] Consequently they have attributed the failure of their calculations to NCMET (rather than to variational collapse).[1] The NCMET charge wave function is composed of a rigorously finite number of configurations, and is well suited for CI calculations.[9-11] The exact NCMET charge wave function, however, is defined as that portion of the exact wave function contributed by a specific set of configurations,[7] and not as a result of the CI calculation based on this set. The result of a CI calculation will be a good approximation to the exact charge wave function only if the coupling between these configurations and the remaining configurations is small,[9] as is usually the case. Furthermore, because NCMET is consistent with the well-established principles of variational theory (for ground as well as for excited states), the fact that one is using some aspect of NCMET does not itself grant a license to ignore these well-established principles. In particular, in the calculations of Nicolaides and Beck,[5,6] merely selecting configurations on the basis of NCMET did not provide any protection against variational collapse. Having suffered variational collapse, the configurational mixing coefficients obtained in their work differ greatly from those in the exact wave function of each state. Consequently, the wave functions calculated by Nicolaides and Beck for these states were not good approximations to the corresponding NCMET charge wave functions, and the resulting inaccurate oscillator strengths calculated by Nicolaides and Beck have nothing to do with NCMET.

The earlier calculations of Öksüz and Sinanoğlu[9] on some of these same states employed the constraint $\zeta_s = \zeta_p = \zeta_d = \frac{5}{3}\zeta_f$. The resulting values of ζ were determined by a local minimum dominated by the d-symmetry virtual orbital. Consequently, the s-symmetry virtual orbitals found in these calculations[9] are very compact, like normal $\hat{f}_s$ semi-internal orbitals, and the $3s$ Rydberg orbital is essentially absent. This is reflected in the *small negative* coefficient of the $1s^22s^22p^2s$ configuration in their $1s^22s2p^{4\,4}P$ wave function. (See the fourth column of Table II of Ref. 2.)

Because the important $3s$ Rydberg configurations have been omitted, the wave functions of Öksüz and Sinanoğlu for the N I ^4P and N II $^1P^0$ are relatively poor approximations compared to most others they calculated. As shown by the f values calculated with these wave functions, however, they are nevertheless substantial improvements over the RHF wave functions, as well as the wave functions subsequently calculated by Nicolaides and Beck. Thus, for the N I $^4S^0$-^4P transition at 1134 Å, for which the experimental measurements[17] indicate an f value of 0.08, we find RHF (length/velocity) results[18] of 0.49/0.56; Öksüz-Sinanoğlu-Westhaus results[18] of 0.14/0.19; and the subsequent Nicolaides-Beck (length) result[6] of 0.29.

In the more recent calculations of Luken and Sinanoğlu,[2,3] NCMET charge wave functions for the states in question were calculated using the HUM theorem to prevent variational collapse. In each case, oscillator strengths calculated using these new wave functions were found to be in much better agreement with accurate experimental results, where available than were the results of all previous calculations. For example, in the case of the nitrogen atom 1134-Å transition, length, and velocity f values of 0.04 and 0.08 were obtained. The difference between the length and velocity results indicates that significant room for improvement remains. It is expected that these results can be improved through the use of the "charge supermultiplet,"[19] as has previously been suggested.[2,3]

Nicolaides and Beck also recently calculated[1,20] some of these wave functions and the associated oscillator strengths. Lacking the wave functions involved in these calculations, as well as the corresponding velocity f values, the accuracy of the calculations is difficult to assess. In order to judge the accuracy, it is interesting to note that Table I of the accompanying Comment,[1] which according to Nicolaides and Beck summarizes the effects of basis sets on the calculations of the oscillator strengths of the 1134-Å transition of the nitrogen atom, omits (a) the velocity result (0.08) of Luken and Sinanoğlu,[2,3] and (b) the length result (0.29) of Nicolaides and Beck.[6]

Finally, we note that Nicolaides and Beck are correct in asserting that NCMET is not a theory of oscillator strengths. NCMET is a theory of the electronic structure of atoms and molecules, and the application of NCMET to the calculation of oscillator strengths is only one facet of NCMET. Thus we find it very encouraging to note that, in the examples cited by Nicolaides and Beck,[1] the results of calculations based on NCMET are always at least as accurate, and usually more accurate, than the more-elaborate calculations of the specialized approach recommended by Nicolaides and Beck.[20]

In conclusion, we repeat our claim that certain calculations of Nicolaides and Beck[5,6] have suffered from variational collapse. (I.e., those for the Be I $2p^{2\,1}S$, B I $2s2p^{2\,2}S$, C I $2s2p^{3\,3}P^o$, N II $2s2p^{3\,1}P^o$, N I $2s2p^{4\,4}P$, O II $2s2p^{4\,2}P$, O I $2s2p^{5\,3}P^o$, and the F II $2s2p^{5\,1}P^o$ states.) Consequently the wave functions calculated by Nicolaides and Beck for these states were not NCMET charge wave functions and the resulting oscillator strengths calculated by Nicolaides and Beck have nothing to do with NCMET. Conversely, the wave functions calculated by Nicolaides and Beck for states which were not subject to variational collapse represent good approximations to the corresponding NCMET charge wave functions, and the f values calculated using these wave functions[5,6] represent results of NCMET.

---

[1] C. A. Nicolaides and D. R. Beck, preceding paper, Phys. Rev. A 18, 1307 (1978).

[2] W. L. Luken and O. Sinanoğlu, Phys. Rev. A 13, 1293 (1976).

[3] W. L. Luken and O. Sinanoğlu, J. Chem. Phys. 64, 1495 (1976); 64, 3141 (1976); 64, 4680 (1976).

[4] O. Sinanoğlu, Int. J. Quantum Chem. Suppl. 9, 155 (1975).

[5] C. A. Nicolaides and D. R. Beck, J. Phys. B 6, 535 (1973).

[6] C. A. Nicolaides, Chem. Phys. Lett. 21, 242 (1973).

[7] H. J. Silverstone and O. Sinanoğlu, J. Chem. Phys. 44, 1899 (1966); 44, 3608 (1966).

[8] B. Skutnik, I. Öksüz, and O. Sinanoğlu, Int. J. Quantum Chem. Suppl. 2, 1 (1968).

[9] I. Öksüz and O. Sinanoğlu, Phys. Rev. 181, 42 (1969); 181, 54 (1969).

[10] O. Sinanoğlu, in *Atomic Physics*, edited by B. Bederson, V. W. Cohen, and F. M. S. Pichanick (Plenum, New York, 1969), Vol. I.

[11] W. L. Luken and O. Sinanoğlu, At. Data Nucl. Data Tables 18, 525 (1976).

[12] P. O. Löwdin, Adv. Chem. Phys. 2, 207 (1959).

[13] E. A. Hylleraas and B. Undheim, Z. Phys. 65, 759 (1930); J. K. L. MacDonald, Phys. Rev. 43, 830 (1933).

[14] A. Mukherji and M. Karplus, J. Chem. Phys. 38, 44 (1963); P. S. C. Wang, M. L. Benston, and D. P. Chong,

ibid. 59, 1721 (1973), and additional references cited therein.

[15] H. S. Taylor, Adv. Chem. Phys. 18, 91 (1970).

[16] A. Hibbert, J. Phys. B 6, L127 (1973).

[17] W. Hayden Smith, J. Bromander, L. J. Curtis, and R. Buchta, Phys. Scr. 2, 211 (1970); G. M. Lawrence and B. D. Savage, Phys. Rev. 141, 67 (1966); H. G. Berry, W. S. Bickel, S. Bashkin, J. Desquelles, and R. Schectman, J. Opt. Soc. Am. 61, 947 (1971).

[18] P. Westhaus and O. Sinanoğlu, Phys. Rev. 183, 56 (1969).

[19] O. Sinanoğlu, in *Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet*, edited by C. Sandorfy, P. J. Ausloos, and M. Robin (Reidel, Dordrecht, Holland, 1974).

[20] D. R. Beck and C. A. Nicolaides, Int. J. Quantum Chem. Suppl. 10, 119 (1976).