# Reply to "Hole projection, saddle points, and localization in the theory of autoionizing states"

Kwong T. Chung
*Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202*
(Received 9 October 1991)

In the preceding Comment [C. A. Nicolaides, Phys. Rev. A **46**, 690 (1992)], a few statements have been made in regard to the saddle-point method developed by Chung [Phys. Rev. A **20**, 1743 (1979)]. In this Reply, statements made in the preceding Comment are further discussed to clarify any possible misconceptions.

PACS number(s): 32.80.Dz, 34.80.−i

In the preceding Comment [1], Nicolaides questions the originality of the saddle-point method [2]. He states that the equation for a trial wave function

$$\Psi_0^{\rm tr}=A(1-|1s\rangle\langle 1s|)\psi_0(r_1,r_2,r_3) \tag{1}$$

is the equation he used in 1972 [3] and is exactly the form used in Ref. [2]. In Ref. [3], Hartree-Fock orbitals are used in the formulation. In the saddle-point method, the wave function was constructed [2] with the statement, "by assuming a one-particle orbital wave function $\phi_0$,

$$\Psi=A[1-P_0(r_j)]\psi(r_1,r_2,\ldots,r_j,\ldots,r_N)\ , \tag{2}$$

where

$$P_0(r)=|\phi_0(r)\rangle\langle\phi_0(r)| \tag{3}$$

will be a trial function with the $\phi_0$ vacancy . . . ."

In Ref. [3], there are 47 numbered equations and a few other equations that are not numbered. There are also eight numbered equations in the Appendix. None of these equations resembles Eq. (1).

Reference [3] uses a projection-operator approach that utilizes the operators $Q$, $P=1-Q$, and $QHQ$. $Q$ and $P$ are the projection operators. The wave function in Eq. (1) would imply that $Q=A(1-|1s\rangle\langle 1s|)$. Since $A$ and $(1-|1s\rangle\langle 1s|)$ do not commute, $Q^2\neq Q$. $Q$ cannot be a legitimate projection operator. Hence Eq. (1) contradicts the approach of Ref. [3].

Equation (1) is different from Eq. (2). The $\psi$ in Eq. (2) is not antisymmetrized. The particles in $\psi$ are distinguishable. It is not a stand-alone wave function. The antisymmetrization is carried out after the projection. This has important consequences. One may still consider the $\Psi$ in Eq. (2) as a wave function in the closed-channel space, but it is no longer possible to speak of operators such as $QHQ$. In the saddle-point method there is no $Q$ operator to operate on a physically acceptable $N$-particle wave function. In Ref. [1], an operator $Q$ is defined with restrictive assumptions. The methods are, however, quite different.

A more fundamental conceptual difference between the two methods is that in Ref. [3] it is claimed that a vacancy orbital in a physical system should be identical to the particle orbital. Nicolaides has given a lengthy discussion and justification of this assumption [3]. This is just the opposite of Eq. (2), where the vacancy orbital is different from the particle orbital and the variational principle in quantum mechanics is used to determine $\phi_0$.

The saddle-point method I used is a very specific method. It parametrizes the vacancy orbital and maximizes the energy with respect to the parameters in this orbital. Recently I have discussed the origin of this method [4] and its relation to the Feshbach projection-operator formalism, which has been well developed since the 1960s [5]. I have used this projection-operator approach extensively in 1970–1972 [6] and in subsequent years. For those who are familiar with this formalism, the use of $1-P_0$ as a means to build a vacancy was nothing new. Hence, I would rather not claim originality for Eq. (2). The new feature in the saddle-point method is the parametrization of $\phi_0$ and the maximization of energy with respect to these parameters. Perkins [7], Hahn [8], and Dalgarno and Drake [9] have discussed energy maximization in different contexts. These works are interesting and they can also be developed into other saddle-point methods, but their relation with the saddle-point method in question is probably more distant than that of the papers in Ref. [5].

On the question of "proof of *a theorem*" (not theorems), the proof has been given in Sec. II, not in Sec. IV of Ref. [2]. I am not aware of any weakness in this proof. Chung and Davis [10] also stated that "this theorem is rigorous for one-electron systems. In order to generalize it to many-electron systems, we must resort to the variation principle inherent in quantum mechanics. . . ." I do not know how to make it clearer. Note that for autoionizing states the saddle-point method can only give an approximate solution to the Schrödinger equation because of the absence of the open-channel segment. When using the saddle-point method one is not trying to find an exact solution to a $QHQ$ operator; one is trying to find the best approximation to the Hamiltonian within the inner-shell-vacancy picture [2,10].

The second part of the Comment [1] deals with the existence of the $He^-$ $2s2p^2\ ^2D$ resonance. In 1980 [11], I carried out a saddle-point calculation for the $2s2p^2\ ^2D$ state of $He^-$. In this work I failed to find a solution that lies below the He $2s2p\ ^3P^\circ$ threshold. The dominant configuration of this $^2D$ is $[(2s2p)^3P,np\,]^2D$. The spin of this $np$ electron is antiparallel to both target electrons

 

and the corresponding exchange energy is positive. In the absence of a net Coulomb potential, this exchange interaction becomes very important. As the *np* electron approaches the $2s2p\ ^3P^\circ$ target, the positive exchange energy raises the total energy above the $2s2p\ ^3P^\circ$ threshold. It is not an "unconverged solution." The energy converges nicely to the $2s2p\ ^3P^\circ$ threshold (from above) if we allow the *np* electron to be farther and farther away from the nucleus. It should be pointed out that my calculation only ruled out the possibility that this $^2D$ structure is a Feshbach resonance lying below the $2s2p\ ^3P^\circ$ threshold.

In Ref. [1] it is stated that "a converged multiconfiguration Hartree-Fock solution means that at the particular energy of the continuous spectrum this solution has the largest coefficient in the full expansion of the wave function." If I understand correctly, this means that at the particular energy, Nicolaides finds a solution that generates this energy. He then looks at the expansion coefficient in the expanded wave function. In the case of this $^2D$ state, he finds that the $2s2p^2$ configuration has the largest coefficient in his wave function. He uses a predetermined $3d$ bound orbital; this orbital contains some $\varepsilon d$, but it is different from $\varepsilon d$. By including this $2s^23d$ and $2p^23d$, he obtains the desired energy for the wave function. Thus "the optimized $2s^23d$ and $2p^23d$ configurations simply contribute to the localized $\Psi_0$." In his wave function, no other $2s^2nd$ and $2p^2nd$ were included.

This definition of a "converged solution" is different from what I have used in the past. My interpretation of the converged solution in the quantum-mechanical calculation is that within the accepted constraints of a particular problem, we should try to include any and all possible basis functions (or orbitals) into the wave function. If the energy result remains constant, then the solution is a converged and meaningful solution; otherwise it is not. The reason that we do not include certain basis functions in the wave functions is because we believe they will not affect our result.

My question about Nicolaides's $2s2p^2\ ^2D$ calculation is: why not include the other $2s^2nd$ and $2p^2nd$ orbitals with $n=4,5,6,\ldots$? Do these orbitals in some way conflict with the "state-specified theory" whereas $3d$ does not? If we do include these *nd* orbitals into the wave function, the lowest root of the energy will fall towards the $2s^2$ [more precisely, $(2s^2+2p^2)^1S$] threshold. Therefore, the solution Nicolaides obtained was the result of an incomplete calculation.

In his conclusion Nicolaides states that "$He^-$ $2s2p^2\ ^2D$ is real, regardless of whether it is above or below the He $2s2p\ ^3P^\circ$ threshold." When we use a Feshbach-formalism approach and obtain a resonance above the closed channel, then this channel is no longer a closed channel to the resonance. One must redefine the closed-channel projection operator $Q$ and redo the calculation. I do not dispute the reality of the $^2D$ structure in the experiment. My contention is that we have not proved that it is a Feshbach resonance theoretically.

The last part of the preceding Comment deals with the originality of the saddle-point complex-rotation method [12]. In this reference we stated "the method we used here bears some similarity with that used by Junker and Huang [13] except that we propose the use of an optimized closed-channel basis set with the proper vacancy built in, and a different type of basis function is used for the outgoing partial wave." In other words, the basic approach has already been developed and used by Junker and Huang [13]. The only thing different is how this basic approach is implemented. The use of a saddle-point solution in the closed-channel segment helps the convergence of the complex eigenvalue. From the point of view of theoretical foundations, there was nothing new in Ref. [12]. Most of the theoretical discussion in Ref. [12] had been given before in Junker and Huang [13]; Rescigno, McCurdy, and Orel [14]; and others [15], including Nicolaides and Beck [16]. The paper by Nicolaides and Beck [16] is one of the papers in Ref. [2] of Chung and Davis [12].

This work is supported by the National Science Foundation Grant No. 90-20543 and by INT 91-01761.

[1] C. A. Nicolaides, preceding Comment, Phys. Rev. A **46**, 690 (1992).
[2] K. T. Chung, Phys. Rev. A **20**, 1743 (1979).
[3] C. A. Nicolaides, Phys. Rev. A **6**, 2078 (1972).
[4] K. T. Chung, Phys. Rev. A **42**, 5726 (1990).
[5] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. **128**, 932 (1962); T. F. O'Malley and S. Geltman, *ibid.* **137**, A1344 (1965); J. C. Y. Chen, *ibid.* **156**, 150 (1967); A. K. Bhatia, A. Temkin, and J. F. Perkins, *ibid.* **153**, 177 (1967).
[6] K. T. Chung and J. C. Y. Chen, Phys. Rev. Lett. **27**, 1112 (1971); J. C. Y. Chen, K. T. Chung, and A. L. Sinfailam, Phys. Rev. A **4**, 1517 (1971); K. T. Chung and I. H. Chen, Phys. Rev. Lett. **28**, 783 (1972); K. T. Chung and J. C. Y. Chen, Phys. Rev. A **6**, 686 (1972); K. T. Chung, *ibid.* **6**, 1809 (1972); J. C. Y. Chen and K. T. Chung, *ibid.* **2**, 1892 (1970).
[7] J. F. Perkins, Bull. Am. Phys. Soc. **13**, 80 (1968).
[8] Y. Hahn, Phys. Rev. A **5**, 1607 (1972).
[9] A. Dalgarno and G. W. F. Drake, Chem. Phys. Lett. **11**, 509 (1971).
[10] K. T. Chung and B. F. Davis, in *Autoionization–Recent Developments and Applications,* edited by A. Temkin (Plenum, New York, 1985), p. 73.
[11] K. T. Chung, Phys. Rev. A **22**, 1341 (1980).
[12] K. T. Chung and B. F. Davis, Phys. Rev. A **26**, 3278 (1982).
[13] B. R. Junker and C. L. Huang, Phys. Rev. A **18**, 313 (1978).
[14] T. N. Rescigno, C. W. McCurdy, Jr., and A. E. Orel, Phys. Rev. A **17**, 1931 (1978).
[15] See, e.g., papers in Int. J. Quantum Chem. **14** (4) (1978).
[16] C. A. Nicolaides and D. R. Beck. Int. J. Quantum Chem. **14**, 457 (1978).