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Electron-correlation effects in the positions and widths of two-electron autoionizing resonances

N. Moiseyev and F. Weinhold
Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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Some recent numerical results for complex resonance eigenvalues of the helium isoelectronic sequence are analyzed in terms of $1/Z$ perturbation theory in order to study the physical factors governing resonance lifetimes. It is pointed out that principal trends in the asymptotic behavior of resonance positions and widths can be rationalized in terms of Hund's rules and familiar principles of bound-state electron-correlation theory, particularly in terms of the radial correlations and their third-order coupling to angular correlations. Such analysis shows, for example, why resonance lifetimes may often shorten with increasing Z, even though the $Z = \infty$ (hydrogenic) limit seems to imply an infinite lifetime. The analysis also suggests the possibility of highly correlated, two-electron "bound states" embedded in the continuum for certain critical noninteger values of nuclear charge Z.

I. INTRODUCTION

The finite lifetimes of autoionizing "resonance" states are pure correlation effects. In the absence of electron-electron repulsions, such states would exist indefinitely as bound states in the continuum, subject only to the usual radiative decay processes which limit the lifetime of ordinary bound states below an ionization threshold. Recently, the positions and lifetimes of several atomic and molecular autoionizing resonances have become available from variational calculations based on the complex-scaling formalism.[1] While accurate data of this type are still scant, it is desirable to analyze such results in terms of the physical factors affecting resonance lifetimes, in order to gain a clearer physical picture of the autoionizing process and to guide the construction of variational trial functions which can accurately represent resonance decay. In the present work, correlation effects in autoionizing states of two-electron atoms are studied by analyzing recent variational results in terms of the $1/Z$ perturbation formalism. From this analysis we propose a qualitative picture of the decay process in terms of correlation effects familiar from studies on bound states. Such a picture may serve as a provisional guide to suggest where further data are needed, and to anticipate broad trends in the autoionizing lifetimes of other atomic and molecular systems.

II. ANALYSIS OF RESONANCE EIGENVALUES BY $1/Z$ PERTURBATION THEORY

The resonance position E_r and width (inverse lifetime) Γ of an autoionizing state can be associated with a complex eigenvalue $W = E_r - \frac{1}{2}i\Gamma$ of the complex-scaled Hamiltonian operator $\hat{H}_\theta(\vec{r}) = \hat{H}(re^{i\theta})$

$$\hat{H}_\theta \psi = W\psi\,, \quad W = E_r - \tfrac{1}{2}i\Gamma \tag{1}$$

with square-integrable eigenfunction ψ.[2] In the $1/Z$ perturbation expansion[3] for an atom of nuclear charge Z, $\hat{H}_\theta$ can be written

$$Z^{-2}\hat{H}_\theta = \hat{H}_\theta^{(0)} + Z^{-1}\hat{H}_\theta^{(1)}\,, \tag{2}$$

where

$$\hat{H}_\theta^{(0)} = e^{-2i\theta}\sum_i -\frac{1}{2}\nabla_i^2 - e^{-i\theta}\sum_i \frac{1}{r_i} \tag{3a}$$

$$\hat{H}_\theta^{(1)} = e^{-i\theta}\sum_{i<j}\frac{1}{r_{ij}}\,. \tag{3b}$$

The perturbed energy up to order N is

$$Z^{-2}\tilde{W}^{(N)} = \sum_{n=0}^{N}\frac{W^{(n)}}{Z^n}\,. \tag{4}$$

Since $\hat{H}_\theta^{(0)}$ is of separable hydrogenic form, both $W^{(0)}$ and $W^{(1)}$ are real,[2b,4] so that

$$E_r = Z^2W^{(0)} + ZW^{(1)} + \mathrm{Re}W^{(2)} + Z^{-1}\mathrm{Re}W^{(3)} + O(Z^{-2}) \tag{5a}$$

$$\Gamma = \Gamma^{(2)} + Z^{-1}\Gamma^{(3)} + O(Z^{-2})\,, \tag{5b}$$

with $\Gamma^{(n)} = -2\,\mathrm{Im}W^{(n)}$. The width Γ is non-negative, so that necessarily $\Gamma^{(2)} \geq 0$. It was shown by Simon[2b] that this leading contribution to the width is equivalent to the "Fermi Golden Rule" for the decaying hydrogenic state.

While the leading terms of the expansions (5) might be calculated directly by perturbation theory, we have chosen to fit them to Ho's[5] recent variational calculations for ^1S, $^{1,3}P$ autoionizing resonances of the helium isoelectronic sequence above the $n = 3$ threshold [see Figs. 1(a), 1(b) and 2(a), 2(b)]. Related results for the $2s2p\;^{1,3}P$ resonances were calculated by Drake and Dalgarno[6] by another procedure, and are shown in Figs. 1(c) and 2(c). Graphical analysis of the variational widths leads to the estimates of the perturbation coefficients $\Gamma^{(2)}$, $\Gamma^{(3)}$ summarized in Table I.

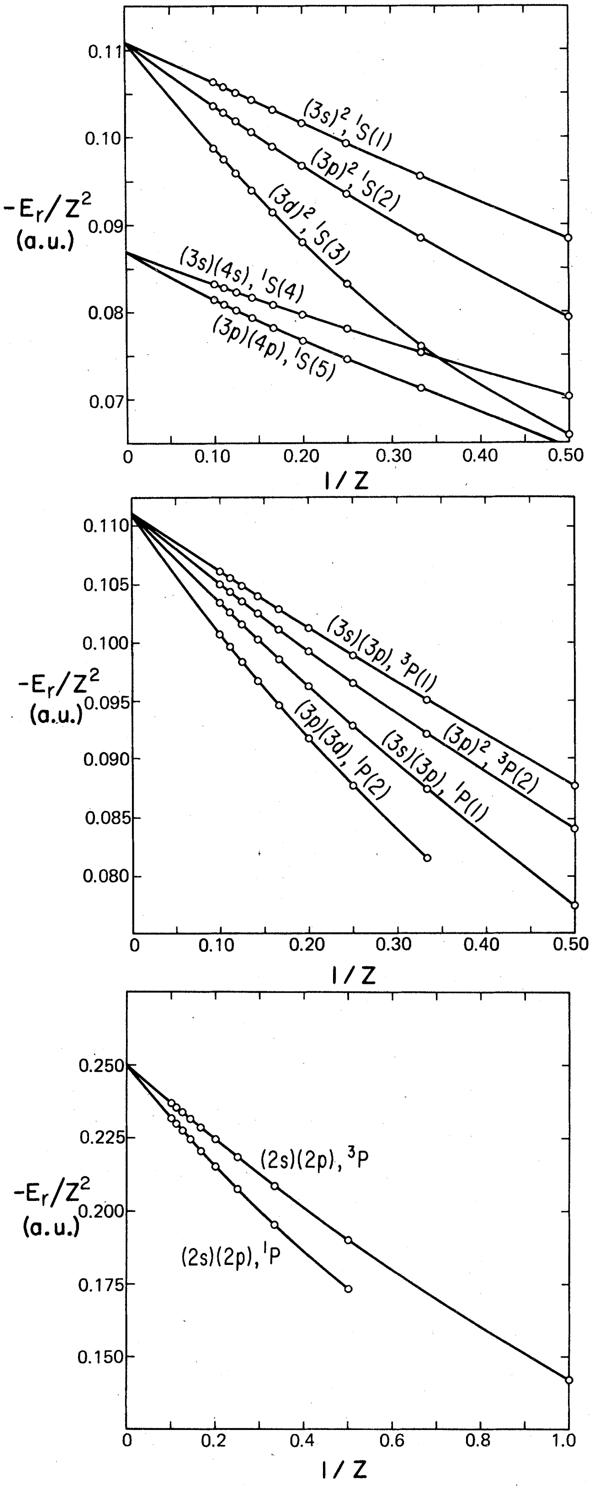

FIG. 1. Resonance positions of the helium isoelectronic sequence, with dominant orbital configuration assigned as described in the text. (a) ${}^1S$ resonances, from the data of Ho (Ref. 5); (b) ${}^{1,3}P$ resonances, from the data of Ho (Ref. 5); (c) $2s2p$, ${}^{1,3}P$ resonances, from the data of Drake and Dalgarno (Ref. 6).

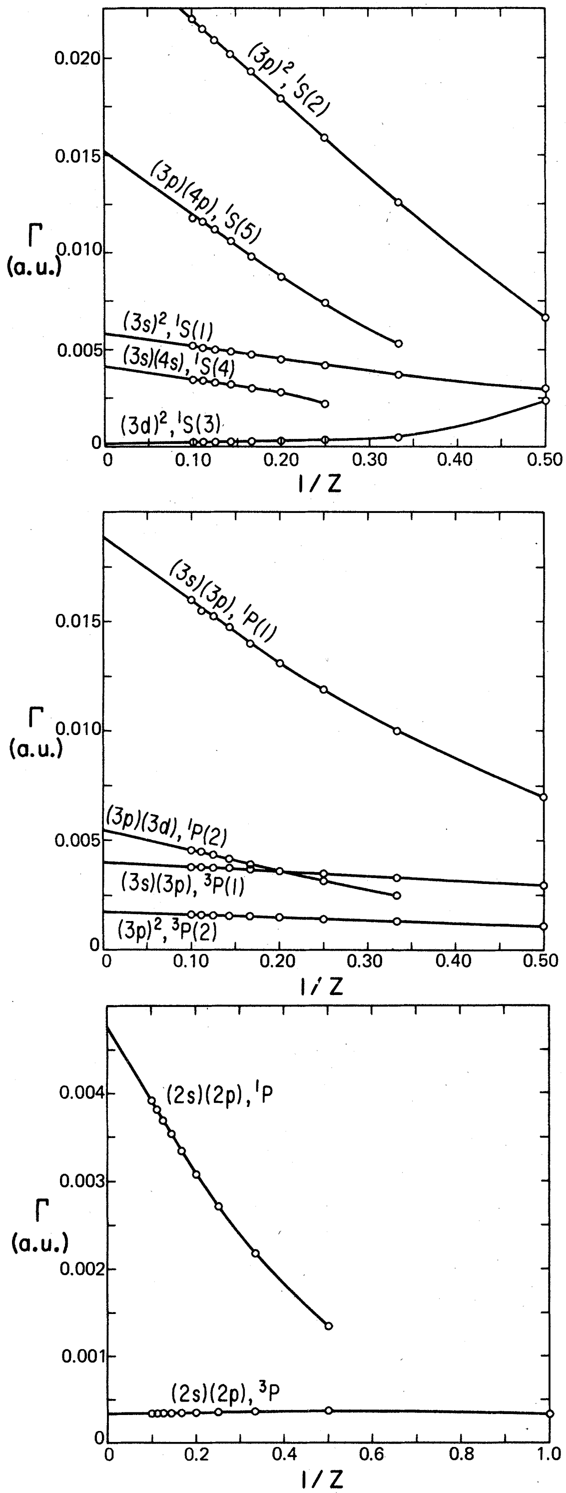

FIG. 2. Resonance widths of the helium isoelectronic sequence, with dominant orbital configuration assigned as described in the text. (a) ${}^1S$ resonances, from the data of Ho (Ref. 5); (b) ${}^{1,3}P$ resonances, from the data of Ho (Ref. 5); (c) $2s2p$, ${}^{1,3}P$ resonances, from the data of Drake and Dalgarno (Ref. 6).

TABLE I. Leading terms in the $1/Z$ expansion of the resonance width, $\Gamma = \Gamma^{(2)} + \Gamma^{(3)} Z^{-1} + O(Z^{-2})$, for the helium isoelectronic sequence.

State	$\Gamma^{(2)}$ (a.u.)	$\Gamma^{(3)}$ (a.u.)
$(3p)^2$, $^1S(2)$	0.026	–0.040
$(3p)(4p)$, $^1S(5)$	0.015	–0.032
$(3s)^2$, $^1S(1)$	0.005_5	-0.006_5
$(3s)(4s)$, $^1S(4)$	0.004_0	-0.007_0
$(3s)(3p)$, $^1P(1)$	0.019	–0.035
$(3p)(3d)$, $^1P(2)$	0.005_5	-0.009_0
$(3s)(3p)$, $^3P(1)$	0.004_0	-0.002_2
$(3p)^2$, $^3P(2)$	0.001_5	-0.001_0
$(2s)(2p)$, ^1P	0.0048	–0.006 6
$(2s)(2p)$, ^3P	0.000 33	+0.000 11

These numerical values form the basis for the analysis given below.

III. RESONANCE POSITIONS

Although Ho's variational resonance states were labeled only by energy order, it is possible to assign the leading electron configuration in each of these states on the basis of the Z^{-1} asymptotic dependence of resonance positions, as plotted in Fig. 1, and familiar rules for the ordering of bound-state levels. As $Z \to \infty$, resonance positions converging toward $E_r = -(\frac{2}{9})\frac{1}{2}Z^2$ must be associated with doubly occupied hydrogenic $n = 3$ levels (e.g., $3s^2$, $3p^2$, or $3d^2$ for ^1S symmetry), while those converging to $E_r = -(\frac{1}{9} + \frac{1}{16})\frac{1}{2}Z^2$ are open-shell states with $n = 3$, $n = 4$ orbitals occupied ($3s4s$, etc.). On the basis of the usual "$n + l$ rule", the ordering of resonances of each type is expected to be[7]

$$E(3s^2) < E(3p^2) < E(3d^2)$$

$$E(3s3p) < E(3p^2) < E(3p3d)$$

$$E(3s4s) < E(3p4p)\,.$$

Each of the states shown in Figs. 1(a) and 1(b) has accordingly been labeled with an electron configuration based on these assignments, together with Ho's original label [$^1S(1)$ for the lowest ^1S resonance, and so on]. It will be seen that these assignments are all consistent with Hund's rules for the ordering of members of a multiplet, so that resonances of triplet spin multiplicity fall below corresponding singlets of the same orbital configuration, and P resonances fall below S resonances. The rationalization of these orderings would be similar to that employed for ordinary bound states, and is not discussed further here.

IV. RESONANCE WIDTHS: SECOND-ORDER CONTRIBUTIONS

Since nonzero resonance widths are a pure correlation effect, it is interesting to see to what extent these widths can be understood in terms of an approximate proportionality $\Gamma \propto E_{\text{corr}}$, to the electronic correlation energy. Correlation effects of two-electron atoms have been extensively analyzed, so that simple predictions of resonance lifetimes should be possible in terms of known principles of bound-state correlation theory.

The physical picture underlying a relationship between electron correlations and resonance lifetime can be sketched as follows: When two electrons occupy a hydrogenic orbit of large radius $\bar{r}$, their correlations will tend to give a "split-shell" state with inner ($r_{\text{inner}} = \bar{r} - \delta$) and outer ($r_{\text{outer}} = \bar{r} + \delta$) orbits, similar to that of H^-. Radial correlation thus tends to drive one electron inward to a low-energy orbit (higher effective nuclear charge, lower effective quantum number), and the other outward to a loosely bound or unbound orbit, from which the electron may escape. Correlation interactions, particularly of *radial* type, which induce this orbital splitting, can thereby cause the original doubly excited state to decay in a finite lifetime, with emission of an electron, to a low-energy state of the ion.

The $1/Z$ expansion (5b) shows immediately that resonance widths should be insensitive to nuclear charge in the limit of large Z, since the leading contribution to Γ is Z independent. This is in accordance with the near constancy of E_{corr} with respect to Z, which follows similarly from the Z independence of the leading (second-order) contribution to the correlation energy.[8,11] The Fermi Golden Rule, $\Gamma \approx \Gamma^{(2)}$, which neglects all Z-dependent terms, would therefore predict that the resonance width is a constant for all members of the isoelectronic sequence, but as Fig. 2 shows, this is not a good approximation for small Z. Note that although the result of setting $Z = \infty$ is to give the uncorrelated hydrogenic approximation (with no resonance states), the asymptotic value of the width for large Z is nevertheless nonzero.

For a given electron configuration, correlation effects are expected to be stronger in singlet states than in triplets, since (following the usual argument) the "Fermi hole"[9] in the latter states is already effective in preventing electrons from being in the same regions of configuration space, and thus from correlating strongly. By a similar argument, the widths of singlet states should generally exceed those of corresponding triplets. This is strongly confirmed in the data plotted in Figs. 2(b) and 2(c) where, for example, the width of the $3s3p\ {}^1P$ resonance is seen to be nearly five times that of the corresponding triplet.

One would expect that E_{corr} for a doubly occupied closed-shell configuration would exceed that of a corresponding open shell (i.e., $n \neq n'$, all else being equal), and therefore also that $\Gamma_{\text{closed}} > \Gamma_{\text{open}}$. This indeed seems to be the case. For example, the widths of $3s^2$ and $3p^2\ {}^1S$ resonances are about 50% greater than the corresponding $3s4s$ and $3p4p$ widths, as shown in Fig. 2. Resonances with configurations $nsn's$ might similarly be expected to be narrower for $n' = n+2, n+3, \ldots$ than for $n' = n+1$. Note that such trends run counter to the naive expectation, familiar from barrier potentials, that resonances of higher energy have shorter lifetimes.

One might similarly anticipate that resonances of higher orbital angular momentum have narrower widths, if the orbital structure is otherwise the same. This would be consistent with the Hund's Rule argument that electron repulsions (and hence, correlation corrections) are less severe in states of larger L.

V. RESONANCE WIDTHS: THIRD-ORDER CONTRIBUTIONS

It is striking that the $\Gamma^{(3)}$ coefficients often exceed $\Gamma^{(2)}$ in the data of Table I. This suggests that low-order perturbation theory is inadequate for such resonances (as has been noted in direct perturbative calculations[4]), and that Fermi's Golden Rule omits significant contributions to the resonance width for low Z. Here we seek to analyze the signs and magnitudes of the observed $\Gamma^{(3)}$ corrections (which give the leading Z-dependent contribution to resonance width), taking account of the expected relationship to radial correlation energy.

It is a familiar result that second-order energy expressions make electron correlation effects independent and additive.[10] This seems generally to result in "overshoot" of E_{corr} at the second-order level, since too much flexibility is introduced if the various types of electron correlating motion are allowed to occur independently. The effect of the third-order terms is then to *couple* these correlations, and thus to correct for the second-order overshoot by a contribution of opposite sign. This is evidently also the situation for the resonance widths, since usually $\Gamma^{(3)} < 0$. However, the unusually large *magnitudes* of the third-order coupling terms are quite striking in the resonance states.

The physical picture of this third-order coupling term can be sketched as follows: In atoms, the dominant correlating motions in second order are of radial ("in-out") and angular type. The first causes the electrons to separate into inner and outer orbits, as described previously, while the second keeps electrons on opposite sides of the nucleus. Each of these effects is exaggerated when considered independently. The effect of the third-order coupling of radial and angular correlations is then to bring the electrons back closer together, for the outermost electron, initially in an orbit corresponding to no coupling of radial and angular correlations, will now "see" the other electron tending to lie *behind* the nucleus, thus "descreening" the nuclear charge. This permits the outer electron to move closer to the nucleus, and to reduce the radial separation that was established in lower order. It is evident that the magnitude of such "angular descreening" corrections should be Z dependent, becoming less important for large Z when the fractional effect is smaller. The coupling of radial and angular correlation was extensively studied by Moiseyev and Katriel,[11] who showed it to be the leading contribution to the Z-dependent correlations in two-electron atoms. Evidently, these third-order effects are still more strongly pronounced in the doubly excited autoionizing states. One may think of the strong angular correlation as tending to *increase* the effective nuclear charge binding each electron to the nucleus, thus lengthening the lifetime of the metastable state.

The results of Moiseyev and Katriel suggested that coupling of radial and angular correlations is more important for diffuse orbitals than for tightly bound ones, more important for singlets than for triplets, and more important for p orbitals than for s orbitals. Similar trends are seen in the third-order widths $\Gamma^{(3)}$ of Table I. However, unlike the bound-state E_{corr}, the resonance widths (which depend most strongly on the *radial* correlations) derive such strong negative contributions from $\Gamma^{(3)}$ that the total width might be reduced to small or vanishing values for sufficiently small Z. For example, crude extrapolation of the data of Fig. 2(a) for the $3p^2\ {}^1S(2)$ state suggests that Γ might vanish in the neighborhood of $Z_{\text{crit}} \approx 1.5$. Such a limiting case would evidently correspond to a bound state embedded in the continuum,[12] as discussed by Wigner and von Neumann, Stillinger, and others.[13] It would be interesting to trace further the fate of several of these resonances for smaller noninteger Z.

VI. CONCLUSIONS

It seems that principal trends in the dependence of resonance lifetimes on nuclear charge, spin multiplicity, orbital angular momentum, and other variables can be crudely understood in terms of general principles of bound-state electron-correlation theory, and a simple physical picture relating the radial correlation energy to the autoionizing decay "mechanism." These trends suggest the importance of corrections to the ordinary second-order (Fermi's Golden Rule) theory of resonance decay, and point to areas where additional data could further clarify the physical picture of such states. It will be interesting to determine whether the outlines of the picture sketched here can be extended to cover the systematics of resonance decay in other atomic and molecular systems.

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[1] See the special complex-scaling issue of the Int. J. Quantum Chem. 14, 4 (1978), as well as B. R. Junker and C. L. Huang, Phys. Rev. A 18, 313 (1978); G. D. Doolen, J. Nuttall, and C. J. Wherry, Phys. Rev. Lett. 40, 313 (1978); T. N. Rescigno, C. W. McCurdy, and A. E. Orel, Phys. Rev. A 17, 1931 (1978); P. Winkler and R. Yaris, J. Phys. B 11, 1 (1978); N. Moiseyev, P. R. Certain, and F. Weinhold, Mol. Phys. 36, 1613 (1978) and Int. J. Quant. Chem. 14, 727 (1978); C. W. McCurdy and T. N. Rescigno, Phys. Rev. Lett. 41, 1364 (1978); N. Moiseyev and C. T. Corcoran (to be published).

[2] (a) E. Balslev and J. M. Combes, Commun. Math. Phys. 22, 280 (1971); J. Aguilar and J. M. Combes, Commun. Math. Phys. 22, 269 (1971); B. Simon, Commun. Math. Phys. 27, 1 (1972); (b) B. Simon, Ann. Math. 97, 247 (1973).

[3] J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, Adv. Quantum Chem. 1, 255 (1964).

[4] F. Weinhold, J. Phys. Chem. (to be published).

[5] Y. K. Ho, J. Phys. B 12, 387 (1979).

[6] G. W. F. Drake and A. Dalgarno, Proc. R. Soc. London A 320, 549 (1971).

[7] Several other resonance configurations with $n=3$, $n'=4$ would be possible, but were apparently not calculated by Ho. In assigning Ho's $^1S(4)$ and $^1S(5)$ to be $3s4s$ and $3p4p$ (instead of $3d4d$), we implicitly assume that Ho's resonances were the lowest of their symmetry type.

[8] P.-O. Löwdin, Adv. Chem. Phys. 2, 207 (1959); J. Mol. Spectrosc. 3, 46 (1959); J. Linderberg and H. Shull, J. Mol. Spectrosc. 5, 1 (1960).

[9] R. J. Boyd and C. A. Coulson, J. Phys. B 7, 1805 (1974), N. Moiseyev, J. Katriel, and R. J. Boyd, J. Phys. B 8, L130 (1975); N. Moiseyev, J. K. Katriel, and R. J. Boyd, Theor. Chim. Acta 45, 61 (1977).

[10] J. Lennard-Jones and J. A. Pople, Philos. Mag. 43, 581 (1952); P. R. Taylor and R. G. Parr, Proc. Nat. Acad. Sci. U.S.A. 38, 154 (1952); O. Sinanoğlu and K. A. Brueckner, *Three Approaches to Electron Correlation in Atoms* (Yale University, New Haven, Conn., 1970).

[11] N. Moiseyev and J. Katriel, Chem. Phys. 10, 67 (1975).

[12] An exception might occur if $E_r \leq E_{\text{threshold}}$ for Z_{crit}, but this does not seem likely except (possibly) for $2s2p\,^1P$.

[13] See, for example, J. von Neumann and E. Wigner, Phys. Z. 30, 465 (1929); F. H. Stillinger, J. Chem. Phys. 45, 3623 (1966); F. H. Stillinger and D. K. Stillinger, Phys. Rev. A 10, 1109 (1974); F. H. Stillinger and T. A. Weber, Phys. Rev. A 10, 1122 (1974); F. H. Stillinger and D. R. Herrick, Phys. Rev. A 9, 446 (1976); B. Simon, Commun. Pure Appl. Math. 22, 531 (1967); N. Moiseyev and J. Katriel, Theor. Chim. Acta 41, 321 (1976); W. P. Reinhardt, Phys. Rev. A 15, 802 (1977); F. H. Stillinger, Phys. Rev. A 15, 806 (1977).