

Variational Iterative Time Dependent Method for Eigenvalues and Eigenfunctions of the Hamiltonian

Markus Saltzer and Eli Pollak*

Chemical Physics Department, Weizmann Institute of Science, 76100 Rehovot, Israel

Received January 13, 2005

Abstract: Short time information on the time evolution of wave packets is combined with the variational theorem to determine eigenvalues and eigenfunctions. As in the Filter Diagonalization Method the input that is needed is a correlation function and its time derivative. The method is iterative and convergent. The time interval needed is short, for example, the determination of tunneling splitting energies ΔE is obtained in a time interval which is substantially shorter than the Fourier time $2\pi\hbar/\Delta E$. The method is applied to some model problems including determining the ground tunneling state in a quartic double well potential using numerically exact short time results obtained from the semiclassical initial value representation series of the exact propagator. This is another example in which tunneling is obtained using only coherent classical paths. Implications of the method for ab initio computation of molecular electronic energies is discussed.

A central challenge facing theoretical Physicists and Chemists today is the invention of convergent methods for the computation of real time quantum dynamics in “large” systems. The past decade has seen significant progress. Makri and co-workers,^{1,2} using the QUAPI method,³ have managed to compute accurate quantum reaction rates in dissipative systems. Mak, Stockburger, and Grabert^{4,5} have derived and applied exact stochastic Schroedinger equations. The Bohmian formulation of quantum mechanics is also used to compute real time quantum dynamics.⁶ Classical propagation of coherent states is being implemented to study time dependent quantum phenomena.^{7,8} Another approach is the use of multiconfigurational time dependent Hartree methods.⁹ We have recently developed a SemiClassical Initial Value Representation (SCIVR) series expression for the exact propagator and used it to compute numerically exact quantum dynamics¹⁰ as well as “deep” tunneling probabilities.¹¹

In all of these methods, a serious limitation is the extent in time for which accurate results can be obtained. One way of overcoming this limitation is by use of the Filter Diagonalization Method (FDM)^{12,13} where the characteristic time needed is $2\pi\hbar/\bar{E}$ where \bar{E} is the local average level

spacing. The central object in the FDM is the correlation function of an initial state $|\Psi\rangle$ with its time evolved form

$$c(t) = \langle \Psi | K(t) | \Psi \rangle \quad (1)$$

where $K(t) = \exp(-iHt/\hbar)$. Harmonic inversion is then used to represent the correlation function in terms of the eigenvalues of the Hamiltonian. The FDM method is not foolproof, as noted by Mandelshtam,¹³ “the degree of convergence will always be a delicate issue”.

A related topic is what may be broadly termed as ab initio chemistry. Present day technology is impressive. A variety of methods, such as density functional theory,¹⁴ quantum Monte Carlo methods,¹⁵ and basis set methods,¹⁶ are used for the computation of molecular energies, but any improvement would be invaluable. One may thus pose the question, how can one use the information obtained from a short time computation of the correlation function to improve upon existing estimates of the energy. These two themes are the central topics of this letter.

A fundamental building block of ab initio chemistry is the Rayleigh-Ritz functional

$$E[\Psi] = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq \epsilon_0 \quad (2)$$

* Corresponding author e-mail: eli.pollak@weizmann.ac.il.

where ϵ_0 is the ground-state energy of the Hamiltonian H . Inserting the time evolved wave function $K(t)|\Psi\rangle$ as a trial function into the functional will not improve anything, since the Hamiltonian commutes with the propagator. However, if one chooses the linear combination $|\Phi(t)\rangle = |\Psi\rangle + K(t)|\Psi\rangle$, the functional becomes time dependent, provided that the initial state $|\Psi\rangle$ is not an eigenstate of the Hamiltonian.¹⁷

The initial wave packet $|\Psi\rangle$ may be expanded in terms of the eigenfunctions (ψ_n) of the Hamiltonian as $|\Psi\rangle = \sum_{j=0}^{\infty} a_j |\psi_j\rangle$ and $a_j = \langle \psi_j | \Psi \rangle$. The time dependent energy functional then becomes (the eigenvalues of H are denoted as ϵ_n)

$$E[\Phi(t)] = \frac{\sum_{j=0}^{\infty} |a_j|^2 \epsilon_j (1 + \cos(\epsilon_j t / \hbar))}{\sum_{j=0}^{\infty} |a_j|^2 (1 + \cos(\epsilon_j t / \hbar))} \quad (3)$$

showing explicitly, how the time evolution changes the contribution of different states at different times to the energy functional.

Noting that $i\hbar(d c(t)/dt) = \langle \Psi | H K(t) | \Psi \rangle$, assuming that the initial state is normalized ($\langle \Psi | \Psi \rangle = 1$), allows us then to write the energy functional explicitly in terms of the correlation function as

$$E[\Phi(t)] = \frac{E[\Psi] - \hbar \frac{d \operatorname{Im} c(t)}{dt}}{1 + \operatorname{Re} c(t)} \quad (4)$$

Minimization of this functional with respect to the time will lead to an improved estimate of the ground-state energy provided that the ground-state energy is positive. As proof, we consider its short time dependence. Using the notation $E_1[\Psi] = \langle \Psi | H | \Psi \rangle$, one has that $\operatorname{Re} c(t) = 1 - (t^2/2\hbar^2)E_2[\Psi] + o(t^4)$ and similarly $-\hbar(d \operatorname{Im} c(t)/dt) = E_1[\Psi] - (t^2/2\hbar^2)E_3[\Psi] + o(t^4)$. It follows that

$$E[\Phi(t)] = E[\Psi] - \frac{t^2}{4\hbar^2}(E_3[\Psi] - E[\Psi]E_2[\Psi]) + o(t^4) \quad (5)$$

If the spectrum of the Hamiltonian is positive, then one readily finds that $E_3[\Psi] - E[\Psi]E_2[\Psi] \geq 0$ so that for short times, the time dependent functional $E[\Phi(t)]$ can only lead to a lower estimate for the ground-state energy than the original estimate $E[\Psi]$. Since the spectrum of the Hamiltonian is typically bounded from below, one can shift the Hamiltonian by a constant value to ensure that the initial time dependence is convex.

One may now use the variational theorem iteratively. One propagates $c(t)$ until the functional reaches a minimum energy $E[\Phi(t_1)]$ at the time t_1 . One then resets the initial state to be $|\Psi_1\rangle = (1/\sqrt{\langle \Phi(t_1) | \Phi(t_1) \rangle})|\Phi(t_1)\rangle$ and the new time dependent function to be $|\Phi_1(t)\rangle = |\Psi_1\rangle + K(t)|\Psi_1\rangle$.

The new correlation function however can be expressed solely in terms of the previous correlation function. That is

$$c_1(t) \equiv \langle \Psi_1 | K(t) | \Psi_1 \rangle = \frac{c(t) + \frac{1}{2}[c(t-t_1) + c(t+t_1)]}{1 + \operatorname{Re} c(t_1)} \quad (6)$$

while the new functional becomes

$$E[\Phi_1(t)] = \frac{E[\Phi(t_1)] - \hbar \frac{d \operatorname{Im} c_1(t)}{dt}}{1 + \operatorname{Re} c_1(t)} \quad (7)$$

In other words, to carry out the iterative procedure, there is no need to know the wave function, all that is needed is the initial correlation function $c(t)$ albeit for ever increasing times, as one proceeds with the iteration. Due to the convex short time property of the functional, this iterative procedure will usually converge to an eigenstate of the Hamiltonian.

Let us assume for the moment, that we have converged to the ground-state eigenvalue at the time t_0 . The ground-state wave function $|\psi_0\rangle$ is then known in principle by following the time evolution. It is a linear combination of the initial wave function $|\Psi\rangle$ propagated to the set of known discrete propagation times. Thus, its overlap with the initial wave function is given as the corresponding linear combination of the correlation function $c(t)$. To obtain the excited-state energy, one projects out the (normalized) ground-state wave function from the initial state, that is one defines $|\tilde{\Psi}\rangle = |\Psi\rangle - \langle \psi_0 | \Psi \rangle |\psi_0\rangle$. The correlation function $c(t) = \langle \tilde{\Psi} | \hat{K}(t) | \tilde{\Psi} \rangle = c(t) - e^{-i\epsilon_0 t/\hbar} |\langle \Psi | \psi_0 \rangle|^2$ can be expressed in terms of the original correlation function $c(t)$ and the ground-state results only. Moreover, it is known for all the times for which the original correlation function $c(t)$ is known accurately. Therefore one may now repeat the iterative process to obtain the first excited-state eigenvalue and eigenfunction. This can then be continued for the second excited state etc.

We will first consider an almost trivial example, to demonstrate that only short time information is needed. Consider a two-state system with eigenvalues $\epsilon_1 < \epsilon_2$ and respective eigenfunctions $|\psi_1\rangle$ and $|\psi_2\rangle$. The “tunneling splitting” is by definition $\Delta E = \epsilon_2 - \epsilon_1 \ll \epsilon_1, \epsilon_2$. We choose the initial wave packet to be localized in one of the wells, that is $|\Psi\rangle = (1/\sqrt{2})(|\psi_1\rangle + |\psi_2\rangle)$. The associated energy $E[\Psi] = (1/2)(\epsilon_1 + \epsilon_2)$. The correlation function is $c(t) = \exp[-i(E[\Psi]t/\hbar)] \cos[(\Delta E/2\hbar)t]$. The time dependent energy functional is then

$$E[\Phi(t)] = \frac{\epsilon_1 + \epsilon_2 + \epsilon_1 \cos\left(\frac{\epsilon_1 t}{\hbar}\right) + \epsilon_2 \cos\left(\frac{\epsilon_2 t}{\hbar}\right)}{2 + \cos\left(\frac{\epsilon_1}{\hbar}t\right) + \cos\left(\frac{\epsilon_2}{\hbar}t\right)} \quad (8)$$

It has its minimum value at the time $t_1 = \pi\hbar/\epsilon_2$ at which $E[\Phi(t_1)] = \epsilon_1$ immediately giving the ground-state energy. To obtain the excited-state energy, one projects out the ground-state wave function from the initial state, that is one defines $|\Psi_1\rangle = |\Psi\rangle - [1 + c^*(t_1)]/2[1 + \operatorname{Re} c(t_1)]|\Phi(t_1)\rangle = 1/\sqrt{2}|\psi_2\rangle$. Clearly then $E[\Psi_1] = \epsilon_2$, demonstrating that the tunneling splitting is obtained by propagation up to time $t_1 \ll 2\pi\hbar/\Delta E$.

Table 1. Iterative Convergence toward the Ground State of a Model System

| j | E_j | $ a(0) ^2$ | $ a(t_1^j) ^2$ | $ a(t_2^j) ^2$ | $ a(t_3^j) ^2$ |
|-----|---------|------------|-------------------|-------------------|-------------------|
| 1 | 1.00000 | 0.98 | 0.9978 | 0.9997 | 0.99996 |
| 2 | 2.00000 | 0.01 | 0.0019 | 0.0002 | $4 \cdot 10^{-5}$ |
| 3 | 2.52360 | 0.005 | $1 \cdot 10^{-5}$ | $2 \cdot 10^{-7}$ | $1 \cdot 10^{-8}$ |
| 4 | 2.81828 | 0.003 | 0.0001 | $1 \cdot 10^{-5}$ | $2 \cdot 10^{-7}$ |
| 5 | 3.04159 | 0.002 | 0.0002 | $6 \cdot 10^{-5}$ | $6 \cdot 10^{-6}$ |

^a The values of the times t_1 , t_2 , and t_3 at which one finds successive minima of the time dependent energy are 0.605, 0.66, and 0.60, respectively.

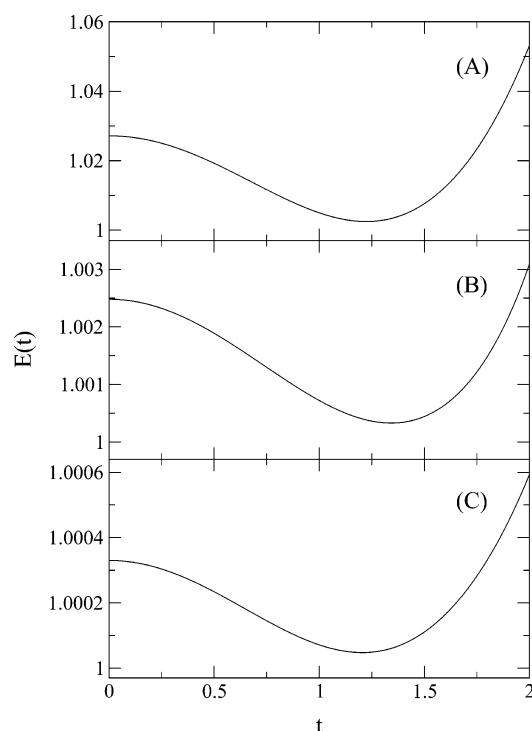


Figure 1. The time dependence of the energy functional for a model ab initio computation. The ground-state energy is 1. The initial value of the average energy, using the initial state as defined in Table 1 was 1.0271. The successive estimates for the energy, as obtained from panels a–c are 1.0025, 1.00033, and 1.000048, respectively.

To demonstrate the utility of the method for ab initio computations, we consider a model spectrum and an initial wave packet which is close to the ground state but slightly contaminated by the excited states. (The eigenvalues and coefficients of the wave packet are given in Table 1.) This would be the typical case of a “good” ab initio computation of the ground-state potential of an atom, which due to computational limitations cannot be converged precisely to the ground state. In Figure 1 we plot the first three iterations for the average energy. Each iteration provides an additional order of magnitude in the accuracy of the ground state. The total integration time needed for this type of accuracy is very short compared to using Fourier transforms.

As a third example, we consider the tunneling split ground state in a symmetric quartic double well potential $V(x) = -1.4x^2 + (1/4)x^4 + 4$. This potential has a pair of bound states whose energies 3.052830 and 3.171736 are below the barrier energy (4). The next bound state is found above the

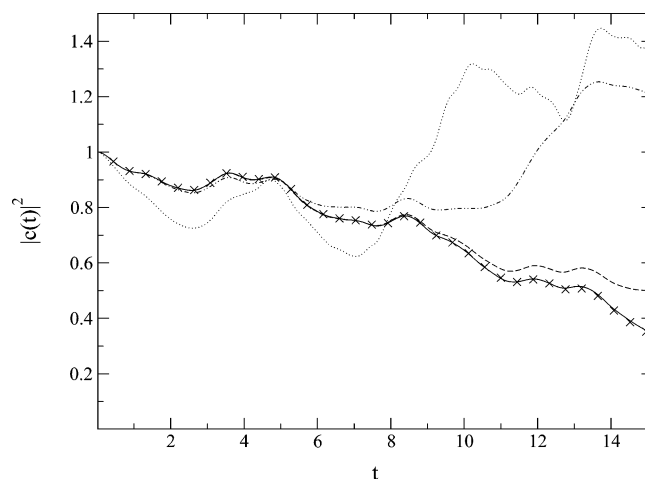


Figure 2. SCIVR series determination of the correlation function $c(t)$. The dotted, dashed–dotted, dashed, and solid lines correspond to inclusion of the 0, 0+1, 0+1+2, 0+1+2+3 terms in the SCIVR series expansion. The crosses show the numerically exact values as obtained from a basis set diagonalization computation.

barrier at $E = 4.536449$. The initial wave packet is taken to be a Gaussian $\langle x | \Psi \rangle = (\alpha/\pi)^{-1/4} \exp[-(\alpha/2)(x - x_0)^2]$ with $x_0 = -1.501$ and $\alpha = 2.806$, centered in the left wall, with average energy $E[\Psi] = 3.1928$.

This one-dimensional quantum problem can be solved numerically exactly using basis set methods. However, here we choose to employ the SCIVR series method,¹⁰ to show explicitly that (a) even if one obtains the correlation function numerically exactly only for short times as is the case when using the SCIVR series method, one may still determine rather accurately the ground tunneling state. The systematic error of truncation of the series is not serious, and (b) the ground-state energy and wave function may be obtained by considering only the real time coherent classical paths.¹¹

Briefly reviewing the SCIVR series method, the quantum propagator is approximated by the Herman-Kluk SCIVR propagator $(K_0(t))$ ¹⁸ which obeys the time evolution equation¹⁹

$$i\hbar \frac{\partial K_0(t)}{\partial t} = HK_0(t) + C(t) \quad (9)$$

where $C(t)$ is a known “correction operator”.¹⁰ The exact quantum propagator may then be represented exactly in terms of a power series in the correction operator $K(t) = \sum_{j=0}^{\infty} K_j(t)$ such that each successive term in the series is obtained from the recursion relation

$$K_{j+1}(t) = \frac{i}{\hbar} \int_0^t ds K_j(t-s)C(s) \quad (10)$$

The width parameter chosen for the coherent state appearing in K_0 is $\gamma = 2.5$ chosen by minimizing the expectation value of the correction operator, as described in ref 10c. The absolute value squared of the resulting correlation function $c(t) = \langle \Psi | K(t) | \Psi \rangle$ obtained for increasing order in the SCIVR series is compared in Figure 2 with the numerically exact results obtained using matrix diagonalization. As shall be also shown below, it suffices to go only up to the third

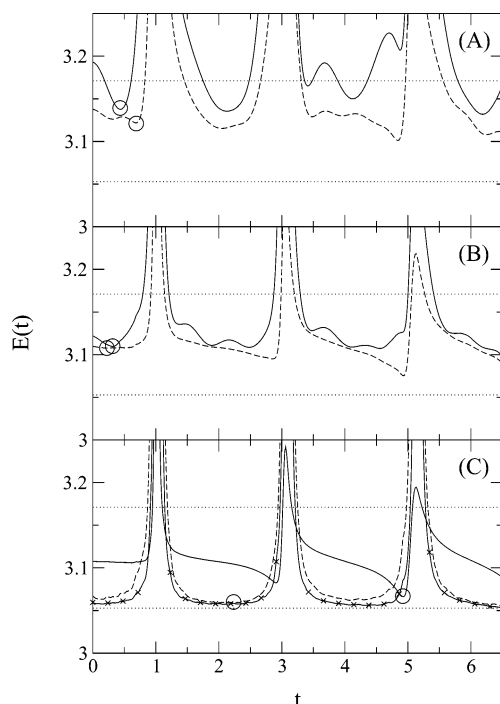


Figure 3. The iterative variational method for computing the ground-state tunneling energy in a double well quartic potential. Panel a shows the zeroth and first iteration. The small circles denote the respective time dependent minima, $t_1 = 0.435$ for the zeroth order functional and then $t_2 = 0.69$ for the first iterated functional. Panel b shows the same for the next two iterations ($t_3 = 0.315$, $t_4 = 0.225$), and panel c shows the final two iterations ($t_5 = 4.92$, $t_6 = 2.235$). The horizontal dotted lines denote the ground and first excited-state eigenvalues as determined by matrix diagonalization of the Hamiltonian. The line with crosses in panel (c) shows the energy after the sixth iteration.

order in the series to obtain results sufficiently accurate for determining the ground-state energy.

In Figure 3 we then show how the correlation function may be used to estimate the ground-state energy via the energy functional. Six iterations suffice to determine that at $t_1 = 2.07$ the ground-state eigenvalue is 3.057352 (a seventh iteration gives 3.054693), to be compared with the numerically exact value 3.052830. The total time interval needed for this determination is $t = 10.89$ which is substantially shorter than the Fourier time $t = 2\pi/\Delta E = 52.84$. One notes, that when convergence is obtained, the time dependent energy becomes rather insensitive to the time, except for short time intervals in which the ground-state contribution to the energy functional vanishes (as may be inferred from eq 3 these times are $\sim (2n + 1)\pi/\epsilon_0$, $n = 0, 1, \dots$), and then the functional becomes large compared to the ground-state energy. The energy interval between successive maxima thus also provides information on the ground-state energy. The resulting ground-state wave function, obtained by following the time evolution through the iteration scheme $(N_0|\psi_0\rangle = (1 + \sum_{i=1}^6 K(t_i) + \sum_{i < j}^6 K(t_i + t_j) + \dots + K(t_1 + t_2 + \dots + t_6))|\Psi\rangle$ where the t_i 's are the successive iteration times) is shown in Figure 4.

In summary, we have shown how the variational theorem may be used to determine eigenvalues of Hamiltonian

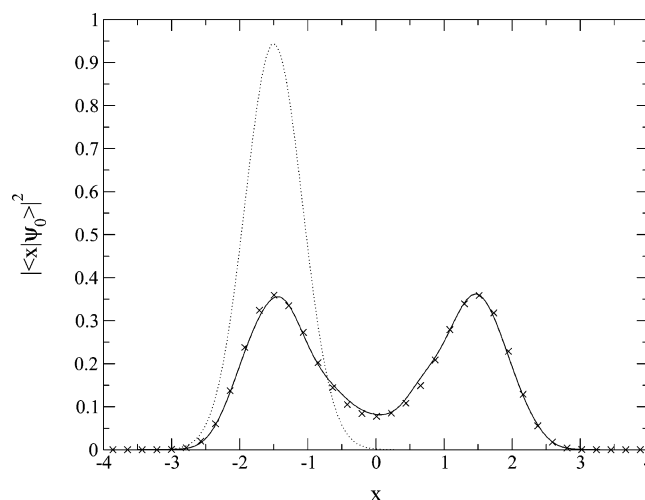


Figure 4. The ground-state tunneling wave function as determined from the iterative variational method. The crosses denote the numerically exact wave function obtained using the standard basis set method. The dotted line shows the initial Gaussian wave function $|\langle x|\Psi_0\rangle|^2$.

systems using short time quantum dynamics data. We have also shown that use of the SCIVR series method leads to convergent eigenvalues and that one does not need to go to a very high order in the series to obtain convergence. This methodology should be useful for extending the accuracy of ab initio computations of electronic energies, using the “best” available ab initio wave function combined with a short time quantum propagation. We have shown that this strategy ensures an even better estimate of the ground-state energy. The same methodology can then be used also to estimate the first excited-state energy. This would be a significant step forward in the implementation of ab initio technology for spectroscopy. Although in principle one could obtain the whole spectrum, each additional excited state demands an increasingly more accurate determination of the previous eigenvalues which in turn will demand longer time propagation which at some point will become prohibitive. Finally, we note that use of the variational method presented here does not suffer from the ambiguities of the nonlinear harmonic inversion method which are found in the FDM method.

Acknowledgment. M.S. gratefully acknowledges a Minerva Foundation (Munich) fellowship. This work has also been supported by grants of the U.S.–Israel Binational Science Foundation and the Israel Science Foundation. The PACS classification is 03.65.Sq, 03.65.Xp, 31.10.+z, 31.15.-p, 31.15.Gy.

References

- (1) Topaler, M.; Makri, N. *J. Chem. Phys.* **1994**, *101*, 7500.
- (2) Topaler, M.; Makri, N. *J. Phys. Chem.* **1996**, *100*, 4430.
- (3) Makri, N. *Chem. Phys. Lett.* **1992**, *193*, 435.
- (4) Stockburger, J.; Mak, C. H. *J. Chem. Phys.* **1999**, *110*, 11.
- (5) Stockburger, J.; Grabert, H. *Phys. Rev. Lett.* **2002**, *88*, 170407.

- (6) Wyatt, R. E. *J. Chem. Phys.* **2002**, *117*, 9569. Babyuk, D.; Wyatt, R. E.; Frederick, J. H. *J. Chem. Phys.* **2003**, *119*, 6482. Hughes, K. H.; Wyatt, R. E. *J. Chem. Phys.* **2004**, *120*, 4089.
- (7) Shalashilin, D. V.; Child, M. S. *J. Chem. Phys.* **2000**, *113*, 10028. Shalashilin, D. V.; Child, M. S.; Clary, D. C. *J. Chem. Phys.* **2004**, *120*, 5608.
- (8) Burant, J. C.; Batista, V. S. *J. Chem. Phys.* **2002**, *116*, 2748.
- (9) Beck, M. H.; Jaeckle, A.; Worth, G. A.; Meyer, H.-D.; Kuehn, O. *Phys. Rep.* **2000**, *324*, 1. Wang, H.; Thoss, M. *J. Chem. Phys.* **1289**, *119*, 2003.
- (10) Pollak, E.; Shao, J. *J. Phys. Chem. A* **2003**, *107*, 7112. Zhang, S.; Pollak, E. *Phys. Rev. Lett.* **2003**, *91*, 190201; *J. Chem. Phys.* **2003**, *119*, 11058; *J. Chem. Phys.* **2004**, *3384*, 121.
- (11) Zhang, D.-H.; Pollak, E. *Phys. Rev. Lett.* **2004**, *93*, 140401.
- (12) Wall, M. R.; Neuhauser, D. *J. Chem. Phys.* **1995**, *102*, 8011.
- (13) Mandelshtam, V. A. *Prof. Nuc. Magn. Res. Spectrosc.* **2001**, *38*, 159.
- (14) Geerling, P.; De Proft, F.; Langenaeker, W. *Density Functional Theory, A bridge Between Chemistry and Physics*; VUB University Press: Brussels, 1999.
- (15) Bernu, B.; Ceperley, D. M.; Lester, W. A. *J. Phys. Chem.* **1990**, *93*, 552; *J. Phys. Chem.* **1991**, *95*, 7782.
- (16) Roos, B. O. *Adv. Chem. Phys.* **1987**, *69*, 399.
- (17) A more general choice would be $|\Phi(t)\rangle = |\Psi\rangle + \alpha K(t)|\Psi\rangle$. Varying the functional with respect to α shows that it is stationary for $\alpha = 1$.
- (18) Herman, M. F.; Kluk, E. *Chem. Phys.* **1984**, *91*, 27.
- (19) Ankerhold, J.; Saltzer, M.; Pollak, E. *J. Chem. Phys.* **2002**, *116*, 5925.

CT0500085