

Adiabatic connection for near degenerate excited states

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(Received 25 November 2003; published 25 May 2004)

In density functional theory, the adiabatic coupling may be treated perturbatively. This Görling-Levy perturbation theory can be applied to both nondegenerate and degenerate states. Formulas are given to second order. Some excitations are shown to be poorly described to first order (i.e., in exact exchange), no matter how weakly correlated the system is. Results are demonstrated on a simple model system, two fermions in a one-dimensional parabolic well with a contact interaction.

DOI: 10.1103/PhysRevA.69.052510

PACS number(s): 31.15.Ew, 31.25.Jf, 31.15.Md, 71.15.Qe

I. INTRODUCTION

Kohn-Sham density functional theory (DFT) is an efficient and widely used method for calculating electronic structure [1,2]. With a sufficiently accurate approximation to the unknown exchange-correlation energy, one can calculate the ground-state density and energy of a system, which provides a great deal of information about its structure and thermo chemistry [3]. However, there is also great interest in excited state properties, such as the overall optical spectrum, individual oscillator strengths [4], and scattering properties [5]. Although in principle all excited state properties can be obtained from the ground state density, in practice several different density functional approaches are used [6]. Some DFT methods for obtaining excited states are difference of self consistent fields (Δ SCF) [7,8], DFT for ensembles [9,10], Görling-Levy perturbation theory (GLPT) [11], variation of bifunctionals [12], and time-dependent DFT (TD-DFT) [13].

TDDFT is an extension of ground state DFT to time-dependent external potentials [13]. Excitation energies of atoms, molecules, and solids can be found as the poles in frequency-dependent linear response susceptibilities [14], or, more practically, as the solution of an eigenvalue equation, which makes the calculation feasible with a Kohn-Sham (KS) orbital basis [15]. In the linear response calculation, the exact exchange-correlation kernel, which is the functional derivative of the exchange-correlation potential, is unknown, so approximations are made. Almost all calculations use an adiabatic approximation, such as the adiabatic local density approximation (ALDA), which ignores the frequency dependence of the kernel. This causes double (and multiple) excitations to be missed [16].

On the other hand, the adiabatic connection, in which the electron-electron repulsion strength is varied keeping the density fixed [17,18], provides a continuous connection from the KS noninteracting system to the fully interacting system. For ground states, the adiabatic connection has been used to find exact conditions satisfied by the unknown exact exchange-correlation energy which have been helpful in constructing accurate approximations. In particular, nonempirical hybrid schemes are obtained via the adiabatic connection [19,20].

Perturbation theory in the adiabatic coupling constant α is called Görling-Levy perturbation theory [11]. GLPT is usually developed for the correlation energy $E_C[n]$ of a finite-density system. The difference between GLPT and the usual perturbation theory is that GLPT constrains the external potential to keep the ground-state density $n(\mathbf{r})$ fixed for all $\alpha \geq 0$. The high-density limit of the correlation energy can then be obtained from the coupling-constant perturbation expansion [11]. By using the optimized effective potential (OEP) method [21] and GLPT, the exchange-correlation energy E_{XC} can be expanded in powers of α , $E_{XC} = \alpha E_X[n] + \alpha^2 E_C^{(2)} + \dots$. Then E_X and $E_C^{(2)}$ can be expressed in terms of KS orbitals, and the corresponding potential $v_X(\mathbf{r}) = \delta E_X / \delta n(\mathbf{r})$ and $v_C^{(2)}(\mathbf{r}) = \delta E_C^{(2)} / \delta n(\mathbf{r})$ can be calculated [22–24].

Assuming the energetic ordering of eigenstates is preserved along the adiabatic connection, i.e., when going from the noninteracting system at $\alpha=0$ to the fully interacting system at $\alpha=1$, the coupling constant path establishes a continuous connection from a given eigenstate of the KS system to one of the physical system, and we can use the adiabatic connection to extract the excited state energies [6]. Fillipi *et al.* applied first order perturbation theory in the adiabatic connection to some real atoms and obtained excitation energies that are better than those resulting from the usual first order perturbation theory [25].

In other work, second-order results have been calculated for the ground state, but only the first order formula has been derived for the excited states. Here we use second order perturbation theory and the adiabatic connection in DFT to calculate the energies of nearly degenerate excited states. We discuss cases where the degenerate treatment is vital. In Sec. II, we introduce the adiabatic connection and give the second order approximation to the excitation energy. In Sec. III, we use a simple one-dimensional model, which contains two particles in a harmonic well interacting via a δ function, to show how to apply the adiabatic connection to the nondegenerate and near degenerate excited states. Our conclusions are given in Sec. IV. We use atomic units throughout ($e^2 = \hbar = m_e = 1$).

II. GENERAL THEORY

The adiabatic connection provides a useful link between the non-interacting KS system and the fully interacting, real system. An α -dependent Hamiltonian is defined as

$$\hat{H}^\alpha = \hat{T} + \alpha \hat{V}_{ee} + \hat{V}_{\text{ext}}^\alpha, \quad (1)$$

where $\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2$, $\hat{V}_{ee} = \sum_{i<j} |\mathbf{r}_i - \mathbf{r}_j|^{-1}$, $\hat{V}_{\text{ext}}^\alpha = \sum_{i=1}^N v_{\text{ext}}^\alpha(\mathbf{r}_i)$, N is the number of electrons, α is the coupling constant, and $v_{\text{ext}}^\alpha(\mathbf{r})$ is the local external potential chosen to keep the ground state density independent of α . At $\alpha=0$, we have the KS system, while at $\alpha=1$, we get the real system. The correlation energy is now α dependent, $E_C^\alpha[n]$, with the true value at $\alpha=1$. The potential in the adiabatic connection formula can be written as [11]

$$v_{\text{ext}}^\alpha(\mathbf{r}) = v_S(\mathbf{r}) - \alpha[v_H(\mathbf{r}) + v_X(\mathbf{r})] - v_C^\alpha(\mathbf{r}), \quad (2)$$

where the KS potential $v_S(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{XC}}(\mathbf{r})$, Hartree potential $v_H(\mathbf{r}) = \int d^3r' n(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$, exchange-correlation potential $v_{\text{XC}}(\mathbf{r}) = \delta E_{\text{XC}}/\delta n(\mathbf{r})$, and

$$v_C^\alpha(\mathbf{r}) = \frac{\delta E_C^\alpha}{\delta n(\mathbf{r})}. \quad (3)$$

All quantities take on their usual values and significance at $\alpha=1$. Thus, we have

$$\hat{H}^\alpha = \hat{H}_S + \alpha(\hat{V}_{ee} - \hat{V}_{\text{HX}}) - \hat{V}_C^\alpha, \quad (4)$$

where $\hat{H}_S = \hat{T} + \hat{V}_S = \hat{H}^{\alpha=0}$ is the Hamiltonian of the KS system, $\hat{V}_{\text{HX}} = \sum_{i=1}^N v_H(\mathbf{r}_i) + v_X(\mathbf{r}_i)$ and $\hat{V}_C^\alpha = \sum_{i=1}^N v_C^\alpha(\mathbf{r}_i)$.

Görling and Levy [11] developed a perturbation theory in powers of α , the density functional analog of Møller-Plesset (MP) perturbation theory [26]. In the standard perturbation theory, $\alpha(\hat{V}_{ee} - \hat{V}_{\text{HX}}) - \hat{V}_C^\alpha$ is the perturbation term, so to first order,

$$E_j^\alpha = E_{Sj} + \alpha \langle \Phi_{Sj} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{Sj} \rangle - \langle \Phi_{Sj} | \hat{V}_C^\alpha | \Phi_{Sj} \rangle. \quad (5)$$

The chief difference in GLPT is that the potential itself changes with α , the perturbation parameter. Using perturbation theory for nondegenerate states, we expand the energy of any eigenstate to second order in α ,

$$E_j^\alpha = E_{Sj} + \alpha \langle \Phi_{Sj} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{Sj} \rangle + \alpha^2 \times \left\{ \sum_{m \neq j} \frac{|\langle \Phi_{Sj} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{Sm} \rangle|^2}{E_{Sj} - E_{Sm}} - \langle \Phi_{Sj} | \hat{V}_C^{(2)} | \Phi_{Sj} \rangle \right\}, \quad (6)$$

(nondegenerate)

where E_S and Φ_S are the energy and wave function of the KS system, respectively. Note that here the perturbation is α dependent. There are two terms of order α^2 in the equation above. In our example, we will show that both of them are important and neither can be ignored.

We can write the transition frequency as the difference of energies. For a non degenerate single excitation, the transition frequency can be expanded in power of α :

$$\omega = \omega_S + \alpha \omega^{(1)} + \alpha^2 \omega^{(2)} + \dots, \quad (7)$$

where

$$\omega^{(1)} = \langle \Phi_{Sj} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{Sj} \rangle - \langle \Phi_{S0} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{S0} \rangle, \quad (8)$$

$$\omega^{(2)} = \sum_{m \neq j} \frac{|\langle \Phi_{Sj} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{Sm} \rangle|^2}{E_{Sj} - E_{Sm}} - \langle \Phi_{Sj} | \hat{V}_C^{(2)} | \Phi_{Sj} \rangle - \sum_{m \neq 0} \frac{|\langle \Phi_{S0} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{Sm} \rangle|^2}{E_{S0} - E_{Sm}} + \langle \Phi_{S0} | \hat{V}_C^{(2)} | \Phi_{S0} \rangle. \quad (9)$$

We compare to the result from TDDFT [4]:

$$\omega = \omega_q + \alpha [q | f_{\text{HX}} | q] + \alpha^2 \left\{ [q | f_C^{(2)} | q] + 2 \sum_{q \neq q'} \frac{\omega_{q'} | [q | f_{\text{HX}} | q'] |^2}{\omega_q^2 - \omega_{q'}^2} + [q | f_{\text{HX}}(\omega_q) | q] \left[q \left| \frac{\partial f_{\text{HX}}(\omega_q)}{\partial \omega} \right| q \right] - \frac{| [q | f_{\text{HX}}(\omega_q) | q] |^2}{2\omega_q} \right\}, \quad (10)$$

where q is a double index, representing a transition from occupied KS orbital i to unoccupied KS orbital a , ω_q is the KS transition frequency, $\Phi_q(\mathbf{r}) = \phi_i^*(\mathbf{r}) \phi_a(\mathbf{r})$, f_{HX} is the Hartree-exchange-correlation kernel, and $[q | f_{\text{HX}}(\omega) | q] = \int d^3r \int d^3r' \Phi_q^*(\mathbf{r}) f_{\text{HXC}}(\mathbf{r}, \mathbf{r}'; \omega) \Phi_q(\mathbf{r}')$. These two expressions are both exact as expansions in powers of α , so they must be identical term by term. Gonze and Scheffler has shown that the first order of α terms are equal [27]. Here we point out that the α^2 coefficients are also equal to each other, although there is no simple relationship among individual terms.

For degenerate-(or nearly degenerate) states, perturbation theory fails if $\langle \Phi_{Sj} | \hat{V}_{ee} - \hat{V}_{\text{HX}} | \Phi_{Sm} \rangle$ is nonvanishing while E_{Sj} and E_{Sm} are equal or close. So we diagonalize the perturbation matrix in the subspace of the degenerate states first, and choose the new base kets that diagonalize the matrix. After that, we apply the formula from the nondegenerate theory, Eq. (6), and the contribution from the subspace of the degenerate states will vanish automatically in the summation.

Consider two KS states $|1\rangle$ and $|2\rangle$ with KS energies E_1 and E_2 that are nearly degenerate. We diagonalize the perturbation matrix

$$\begin{vmatrix} \langle 1 | H_S + \alpha(V_{ee} - V_{\text{HX}}) | 1 \rangle & \langle 1 | H_S + \alpha(V_{ee} - V_{\text{HX}}) | 2 \rangle \\ \langle 2 | H_S + \alpha(V_{ee} - V_{\text{HX}}) | 1 \rangle & \langle 2 | H_S + \alpha(V_{ee} - V_{\text{HX}}) | 2 \rangle \end{vmatrix} \quad (11)$$

to find two eigenvalues E_\pm , and the corresponding normalized eigenstates $|\Phi_\pm\rangle$, that are both linear combinations of $|1\rangle$ and $|2\rangle$:

$$E_\pm(\alpha) = \bar{E} + \alpha \Delta \bar{v} \pm \sqrt{\Delta^2(\alpha) + \alpha^2 \Delta v_{12}^2}, \quad (12)$$

where $\bar{E} = (E_1 + E_2)/2$, $\Delta \bar{v} = (\Delta v_{11} + \Delta v_{22})/2$, $\Delta v_{ij} = \langle i | \hat{V}_{ee} - \hat{V}_{\text{HX}} | j \rangle$ and

$$\Delta(\alpha) = \frac{1}{2}[E_1 - E_2 + \alpha(\Delta v_{11} - \Delta v_{22})], \quad (13)$$

The new eigenstates are

$$|\Phi_+\rangle = \cos \theta |1\rangle + \sin \theta |2\rangle \quad (14)$$

and

$$|\Phi_-\rangle = -\sin \theta |1\rangle + \cos \theta |2\rangle, \quad (15)$$

where

$$\tan 2\theta = \alpha \Delta v_{12} / \Delta(\alpha). \quad (16)$$

Now $|\Phi_\pm\rangle$ are the new basis of the subspace of the near degenerate states, and satisfy $\langle \Phi_+ | \hat{H}_S + \alpha(\hat{V}_{ee} - \hat{V}_{HX}) | \Phi_- \rangle = 0$, so the perturbed energies for the near degenerate states are

$$E = E_\pm(\alpha) - \alpha^2 \langle \Phi_\pm | \hat{V}_C^{(2)} | \Phi_\pm \rangle + \alpha^2 \sum_{m \neq 1,2} \frac{|\langle \Phi_\pm | \hat{V}_{ee} - \hat{V}_{HX} | \Phi_{S_m} \rangle|^2}{E_\pm - E_{S_m}} + \dots (\text{degenerate}). \quad (17)$$

Note that if $|\alpha \Delta v_{12}| / \Delta(\alpha) \ll 1$, $|\Phi_\pm\rangle$ will become $|1\rangle$ and $|2\rangle$ and Eq. (6) is recovered; otherwise, we must use the degenerate formula. Note also that the α dependence of $E_\pm^{(\alpha)}$ is more complex than a simple power series.

Lastly, we apply Eq. (17) to a very specific case, namely two states that become degenerate when $\hat{V}_{ee} = 0$. In such a case, if the electron-electron repulsion is weak, i.e., write $\lambda \hat{V}_{ee}$ with $\lambda \ll 1$, then $\Delta \sim O(\lambda)$ and $\Delta v_{12} \sim O(\lambda)$, so that $\Delta v_{12} / \Delta(\alpha=1) \rightarrow \text{const}$ as $\lambda \rightarrow 0$. If this constant is not small, then Eq. (6) will always fail, no matter how weak the repulsion. Any finite value of λ , no matter how small, breaks the degeneracy in the physical system, and also in the KS system. Even though the exact degeneracy does not occur in the KS system, degenerate perturbation theory is always needed. Thus, even if the ground state is weakly correlated, i.e., its energy is accurately approximated by Hartree-Fock, the nearly degenerate excited states will not be accurately given at this level of approximation.

III. SIMPLE MODEL

Density functional theory applies to any interacting system, whenever a Hohenberg-Kohn theorem can be established [1]. In particular, DFT clearly applies to electrons in any number of dimensions, and interacting with any given repulsion. The details of the functional differ, but the general theorems remain true. In this section, we use a simple one-dimensional model with a δ -function repulsion between the particles. Such a choice makes all the calculations tractable, and the results transparent. Once we draw only conclusions that are independent of the details of the functional, we are on safe ground. In cases where similar calculations have been performed for real atoms, our conclusions agree with those of the realistic applications.

We use a simple model as an example to show how our algorithm works. Two one-dimensional fermions are confined to a parabolic well, and the repulsion between them is a δ function. The Hamiltonian is

$$\hat{H} = -\frac{1}{2} \left(\frac{d^2}{dx_1^2} + \frac{d^2}{dx_2^2} \right) + \frac{1}{2} k(x_1^2 + x_2^2) + \lambda \delta(x_1 - x_2). \quad (18)$$

We use this toy model as an example because it is exactly solvable, and has both non-degenerate and nearly degenerate excited states. We choose $k=1$ without loss of generality. Transforming to center of mass and relative coordinates

$$X = (x_1 + x_2)/2, \quad u = x_1 - x_2, \quad (19)$$

the Schrödinger equation decouples. The center of mass wavefunction is just a harmonic oscillator of mass 2 and frequency 1, and the relative wave function satisfies

$$\left(-\frac{d^2}{du^2} + \frac{1}{4}u^2 + \lambda \delta(u) \right) \phi(u) = \epsilon \phi(u). \quad (20)$$

The total energy is given by

$$E_{Nj} = \epsilon_j + N + 1/2, \quad (21)$$

where $\epsilon_j = j + 1/2$ when $\lambda = 0$, and even for $\lambda \neq 0$, remains the same for odd j because of the node at $u=0$. The even energy eigenvalues of Eq. (20) can be shown to satisfy

$$\lambda = -\frac{2\sqrt{2}\Gamma\left(\frac{3-2\epsilon}{4}\right)}{\Gamma\left(\frac{1-2\epsilon}{4}\right)}, \quad (22)$$

and increase linearly with λ for $\lambda \ll 1$ for even states.

First, we consider the spectrum of our model. For simplicity we discuss only singlet states. We denote the states of the real system as $[N, j]$, where N and j are the quantum numbers in the center of mass and relative coordinates, respectively. The singlet condition implies j must be even. Now we have the ground state $[0, 0]$ in which both the center-of-mass and relative coordinates parts are in their ground states; the first excited state is $[1, 0]$, the second is $[0, 2]$, and the third is $[2, 0]$ where the second and third are close in energy (degenerate at $\lambda=0$), so we need to use the method of nearly degenerate states to treat them. The singlet energy structure atom is shown in Fig. 1.

The exact Kohn-Sham (KS) ground state is easy to calculate for this system. We write the exact wave function

$$\Psi_0(x_1, x_2) = \phi_0(u) \Phi_0(X) \chi_{\text{sing}}, \quad (23)$$

where $\phi_0(u)$ and $\Phi_0(X)$ are the ground-state relative wave function and center-of-mass wave function, respectively. By integrating over one coordinate, we calculate the ground-state density $n(x)$. Then $\phi_{\text{KS}}(x) = \sqrt{n(x)}/2$, and invert the KS equation to calculate $v_S(x) = C - d^2 \phi_{\text{KS}}(x) / 2dx^2$, choosing the constant C so that $v_S \rightarrow kx^2/2$ as $x \rightarrow \infty$. The occupied and unoccupied levels of this potential form the KS system, as shown on the right of Fig. 1.

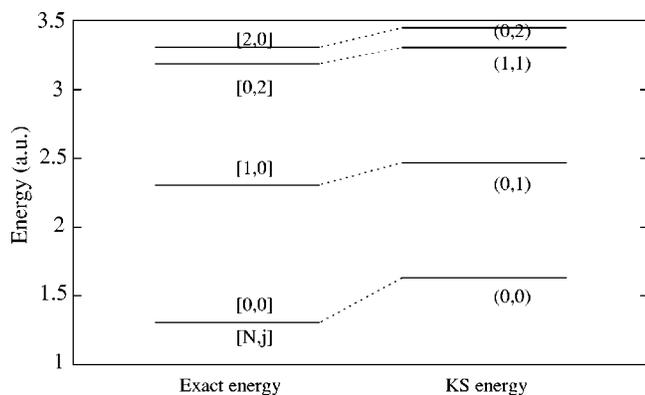


FIG. 1. The lowest singlet levels of our model with $\lambda=1$, both exactly and in the KS system.

In the KS system, we use another notation for the energy levels. We still use two numbers, but they are the KS orbital levels of the two electrons. So, (0,0) is the ground state of the KS system $\phi_0(x_1)\phi_0(x_2)$; and the first excited state is (0,1), which means one electron is on the ground state of the KS orbital while the other is on the first excited state. The KS wave function of this excited state is $[\phi_0(x_1)\phi_1(x_2) + \phi_1(x_1)\phi_0(x_2)]/\sqrt{2}$. For the second excited state, we have a double excited state $\Phi_D = \phi_1(x_1)\phi_1(x_2)$, and the third excited state is the single excited state $\Phi_I = [\phi_0(x_1)\phi_2(x_2) + \phi_2(x_1)\phi_0(x_2)]/\sqrt{2}$. All the KS orbitals are exact.

The ground and first excited states are both nondegenerate, so we can easily apply Eq. (6) to them and find the energies up to second order in α . In practice, it is not straightforward to calculate $v_C^{(2)}(\mathbf{r})$ exactly [28], so we use $v_C^{(2)}(\mathbf{r}) \approx v_C(\mathbf{r})$, an approximation that is valid to the order we need. In the summation over KS states m in Eq. (6), we take the lowest 50 energy levels in the KS system, which we have checked is sufficient for convergence. The second and third excited states are nearly degenerate, so we use Eqs. (11)–(17), where $|1\rangle = \Phi_I$, $|2\rangle = \Phi_D$. In our model system, $\hat{V}_{ee} = \lambda \delta(x_1 - x_2)$, so $\hat{V}_{HX} = \lambda n(x)/2 = \lambda \phi_0^2(x)$, where $\phi_0(x)$ is the ground state orbital of the KS system.

In Table I, we list some approximate results and their errors for our model with $\lambda=0.4$. All energies are referenced to $N+j+1$, the levels at $\lambda=0$. The last two rows labeled “near deg.” in the table are the results from applying the near

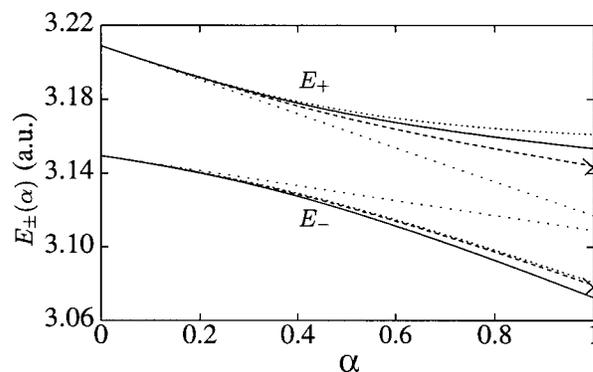


FIG. 2. The adiabatic connection of the second and third excited states energies when $\lambda=0.4$. The crosses indicate the exact energies, the dotted straight lines are first order nondegenerate GLPT, the solid curves are first order near-degenerate GLPT and the dotted curves are the results of standard perturbation theory (first order), and the dashed curves are second order GLPT.

degenerate formula of Eq. (17) to the second and third excited states; the other calculations are done with the nondegenerate formula (6).

The states [0,0], [1,0], [2,0] have the same deviation energy, because they differ only in their center-of-mass excitation. The KS energies listed here are the corresponding ground state (0,0) and the lowest three excited states (0,1), (1,1), (0,2), energies. They are calculated by adding the KS orbitals energies, and then subtracting $N+j+1$. We chose λ sufficiently large to ensure significant differences between the KS and exact levels. The differences are close to 100%. The results from the first order standard perturbation theory are also listed in the table. For the ground and first excited states (both are non-degenerate), they are much closer to the true energies. But the second and third excited states are not as good, because these two states are nearly degenerate. If we apply the nearly degenerate perturbation theory here, better results are achieved. For the GLPT approximation, we calculated first and second order results. From the ground and first excited states, first order GLPT is better than first order standard PT for the nondegenerate states. Keeping the ground-state density fixed plays an important role in the accuracy of the approximation. But for the nearly degenerate states, there is little improvement. Second order near-degenerate GLPT gives the best results in this table. They are

TABLE I. Energy eigenvalues (in a.u.) (relative to harmonic oscillator) for $\lambda=0.4$, i.e., we subtract $N+j+1$ from the energies.

State	Exact energy	KS energy	standard perturbation theory		GL perturbation theory	
			1st order	2nd order	1st order	2nd order
[0,0]	0.143	0.297(100%)	0.156(9%)	0.144(0.8%)	0.144(0.8%)	0.144(0.8%)
[1,0]	0.143	0.223(60%)	0.161(10%)	0.150(5%)	0.144(0.8%)	0.144(0.8%)
[0,2]	0.078	0.149(90%)	0.120(50%)	0.109(40%)	0.084(8%)	0.084(8%)
[2,0]	0.143	0.209(50%)	0.122(-10%)	0.117(-20%)	0.138(-3%)	0.138(-3%)
near deg.	0.078	0.149(90%)	0.081(3%)	0.072(-7%)	0.079(1%)	0.079(1%)
near deg.	0.143	0.209(50%)	0.161(10%)	0.153(7%)	0.144(0.5%)	0.144(0.5%)

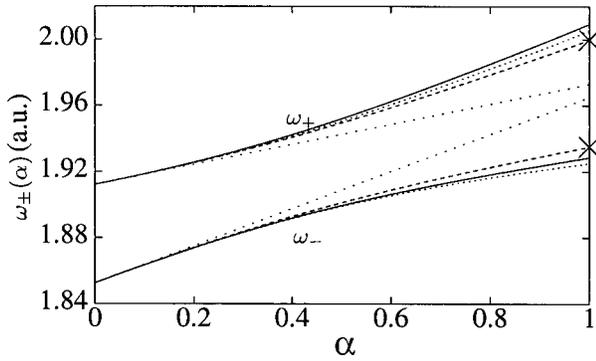


FIG. 3. The adiabatic connection of the transition frequencies when $\lambda=0.4$ for second and third excited states. Notation same as Fig. 2.

better than first order near-degenerate GLPT by an order of magnitude. From the nearly degenerate results, we find that the near-degenerate treatment improves all three perturbation theory approximations.

Fillipi *et al.* calculated the excitation energies of real atoms: He, ionized Li, and Be, from density functional perturbation theory [25]. They compared two kinds of first-order excitation energies, one obtained from the standard perturbation theory without keeping density fixed for all α , as discussed above, and the other to first order in the coupling constant (the same way we get the results of “first order” in GLPT). They found the latter is more accurate. Their conclusion coincides with ours.

We plot the adiabatic connection of the energies and transition frequencies from the ground state to the second and third excited states in Figs. 2 and 3. Compared to the zeroth order approximation ($\alpha=0$, KS system), the first order near-degenerate GLPT approximation has already improved the results a lot. From the standard perturbation results, we see that including $v_C(\mathbf{r})$ alone does not give us a better splitting of the two states. But after adding all the second order terms in Eq. (17), including the sum, we get results very close to the true values. An important property of the second excitation is that the two states are an almost equal mixture of the single and double excitations. If we use TDDFT in the adiabatic approximation, double excitations are missing, and we find only one transition, which is in the middle of the two true transitions [16]. But the double excitation is not a problem in our calculation, since when we diagonalize the per-

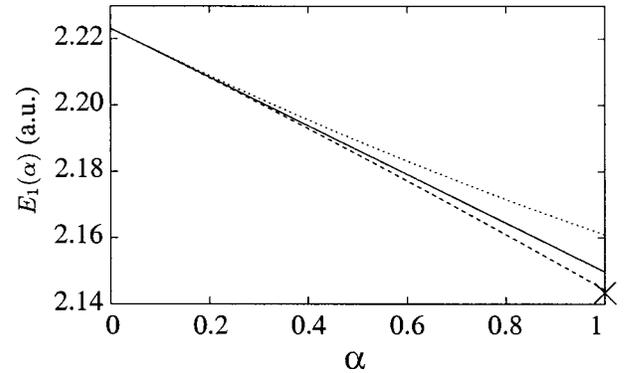


FIG. 4. The adiabatic connection for the energy when $\lambda=0.4$ for the first excited state. The cross indicates the exact energy, the solid line is the first order GLPT approximation, the dotted line is the standard perturbation theory results, and the dashed line is the second order GLPT approximation.

turbation matrix, we have already mixed single and double excitations.

In Fig. 2, we also plot the first order approximation to $E(\alpha)$, at $\lambda=0.4$. The figure shows the results of the first order GLPT approximation of the second excited states if we treat them as nondegenerate states. When λ is small, (and these levels are nearly degenerate,) the first order approximation gives much larger errors than the results if we treat them as near degenerate states. Figure 3 shows that the same conclusions apply to the transition frequencies.

Note that the shape of the curves in Figs. 2 and 3 remains the same no matter how small λ is. In no case will first-order GL perturbation theory be accurate.

Figure 4 shows the energy of the first excited state when $\lambda=0.4$, far from the weak correlation regime. It shows that in Eq. (6), both second order terms in α are important. Here, the first- and second-order GLPT approximations are both close to the true value, but the first-order standard perturbation theory result has a large error in comparison to them. Since the standard perturbation approximation include the first-order GLPT and the $\alpha^2 V_C$ term, but not the summation term, this means sometimes the two terms of the second order in α can cancel each other, so when we calculate to second order in α , we must include them both. This also shows, by keeping the density fixed, GLPT is more accurate than the standard perturbation theory.

From Table I, we can see that when $\lambda=0.4$, we need to use the near-degenerate formula. (At $\lambda=0.4$, $\Delta v_{DI}/d=10.09$.)

TABLE II. Results for $\lambda=1.0$.

State	Exact energy	KS energy	standard perturbation theory		GL perturbation theory	
			First order	Second order	First order	Second order
[0,0]	0.307	0.630(100%)	0.378(20%)	0.304(-0.9%)	0.269(-10%)	0.304(-0.9%)
[1,0]	0.307	0.468(50%)	0.410(30%)	0.306(-0.1%)	0.306(-0.4%)	0.306(-0.1%)
[0,2]	0.187	0.305(60%)	0.300(60%)	0.182(-3%)	0.199(7%)	0.182(-3%)
[2,0]	0.307	0.447(50%)	0.315(3%)	0.319(4%)	0.241(-20%)	0.319(4%)
near deg.	0.187	0.305(60%)	0.206(10%)	0.200(7%)	0.117(-40%)	0.200(7%)
near deg.	0.307	0.447(50%)	0.409(30%)	0.305(-0.7%)	0.324(6%)	0.305(-0.7%)

Now we increase λ to 1, and the value of $\Delta v_{DI}/d$ becomes 4.80. The results are listed in Table II. The near degenerate formula does not give more accurate results here, because higher order terms in α are more significant.

IV. CONCLUSIONS

We have shown how to treat nearly degenerate states in Görling-Levy perturbation theory. The calculated results of the simple model show that for some λ , which corresponds to the electron repulsion constant, the first order approximation is not accurate enough, we need to use the second order approximation which works well for both nondegenerate and (near) degenerate states. In general, for systems with degen-

eracies when $\hat{V}_{ee}=0$, first-order perturbation theory is inaccurate, even if \hat{V}_{ee} is very small.

Although in this paper we have only applied our method to a simple model system, the general results can be extended to real atoms and molecules to calculate excitation energies. For example, the methodology applies to stretched H_2 [29], where the ground- and first excited states are nearly degenerate.

ACKNOWLEDGMENTS

This work was supported by Department of Energy under Grant No. DE-FG02-01ER45928 and National Science Foundation under Grant No. CHE-9731634.

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