

Importance of Nonlocality in the Dynamical Exchange-Correlation Kernel in the Time-Dependent Density Functional Theory

Takada Group

The time-dependent density functional theory (TDDFT) is a powerful tool for studying excitations in atomic, molecular, and condensed-matter systems. In the linear-response regime, the key quantity of TDDFT is the dynamical exchange and correlation (xc) kernel $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$, defined as the Fourier transform of $f_{xc}(\mathbf{r}, \mathbf{r}'; t-t')$ which is given by the functional derivative of the Kohn-Sham xc potential $V_{xc}(\mathbf{r}, t)$ with respect to the electron density $n(\mathbf{r}', t')$. In actual implementation of the theory, we need to resort to some approximation to this quantity. In the absence of its detailed information, the adiabatic local density approximation (ALDA) has been adopted in virtually all calculations so far.

Some years ago, we derived a rigorous formula for obtaining the experimentally observed stopping power, $-dE/dx$, of solids for slow ions in the framework of TDDFT [1], but it turns out that the formula provides a nonzero value for the friction coefficient (or $-dE/dx$ divided by v the velocity of incident ions in the limit of $v \rightarrow 0$) in the homogeneous electron gas with the limit of zero electron density (or in the vacuum), if we adopt ALDA for $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$. This contradictory result urges us to develop a better approximation scheme for this quantity beyond the level of ALDA.

In pursuit of such a scheme, we have reformulated the problem of the stopping power in the framework of the time-dependent current density functional theory (TDCDFT) [2] to find a new interesting rigorous relation between $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ and the tensorial xc kernel, the key quantity in TDCDFT. By invoking the local density approximation to the tensorial xc kernel and exploiting this relation, we have constructed a new approximation form for $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$. The resulting form adds a nonlocal nature to ALDA and the nonlocality is just enough to make the result for the friction coefficient of the electron gas free from the above-mentioned contradiction in the vacuum limit.

In order to check the accuracy of this new form for $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$, we have recalculated the friction coefficient of the homogeneous electron gas at various electron densities and compared the obtained results with the experimental ones. Note that our results for the homogeneous electron gas can be directly compared with the experimental ones in simple metals, in view of the fact that at low velocities the energy loss of ions in solids is due mainly to the stopping power of valence electrons.

In Fig. 1, an example of such comparisons is shown at the electron density as specified by $r_s=2.2$ (r_s : the conventional nondimensional density parameter) corresponding to aluminum with incident ions penetrating from its (111) surface. In the figure, we have also plotted the results in ALDA as well as those

in LDA to the static Kohn-Sham scheme which amounts to the calculation without including any dynamical xc effects.

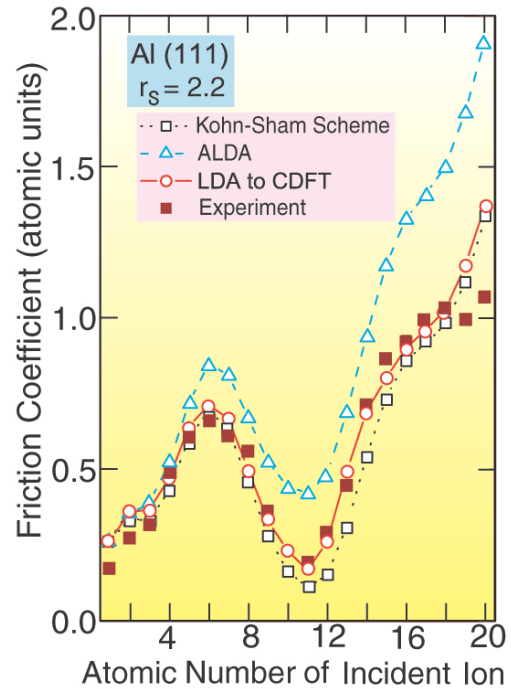


Fig. 1. Comparison between experiment on the friction coefficient of aluminum for slow ions (characterized by the atomic number) obtained at the incident velocity $v=0.5$ atomic units (the solid squares) and theory on the same quantity of the homogeneous electron gas with the electron density equivalent to the valence-electron density in aluminum in the limit of zero ion velocity ($v \rightarrow 0$). The open circles, the open triangles, and the open squares correspond, respectively, to the results in our new approximation scheme (LDA to CDFT), ALDA to $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$, and LDA to the static Kohn-Sham scheme.

As can be seen in Fig. 1, experiment exhibits an oscillatory behavior in the friction coefficient with increasing the atomic number of incident ions. This behavior, which is attributed to the shell structure of valence electrons around the ion, is reproduced well in all the calculation schemes, but the best quantitative agreement with experiment is obtained by our new scheme (namely, LDA to CDFT) for $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$.

We expect that our new approximation form $f_{xc}(\mathbf{r}, \mathbf{r}'; \omega)$ awaits various applications in a wide range of problems concerning dynamical processes in electronic systems.

References

- [1] V. U. Nazarov, J. M. Pitarke, C. S. Kim, and Y. Takada, *Phys. Rev. B* **71**, 121106(R):1-4 (2005).
- [2] V. U. Nazarov, J. M. Pitarke, Y. Takada, G. Vignale, and Y.-C. Chang, *Phys. Rev. B* **76**, 205103:1-6 (2007).

Authors

V. U. Nazarov,^a J. M. Pitarke,^b Y. Takada, G. Vignale^c, and Y.-C. Chang^a

^aAcademia Sinica, Taiwan,

^bEuskal Herriko Unibertsitatea, Spain

^cUniversity of Missouri, USA.